

(12) UK Patent Application (19) GB (11) 2 350 617 (13) A

(43) Date of A Publication 06.12.2000

(21) Application No 9912841.5

(22) Date of Filing 02.06.1999

(71) Applicant(s)
Nissan Chemical Industries Limited
 (Incorporated in Japan)
 7-1 3-chome Kanda-Nishiki-cho, Chiyoda-ku, Tokyo,
 Japan

(72) Inventor(s)
Poopathy Kathirgamanathan
Subramaniam Ganeshamurugan

(74) Agent and/or Address for Service
Kilburn & Strobe
 20 Red Lion Street, LONDON, WC1R 4PJ,
 United Kingdom

(51) INT CL⁷
C08G 73/00 73/02

(52) UK CL (Edition R)
C3R RSM R35D1 R35PX
U1S S1387 S1411 S1424 S1425 S2285

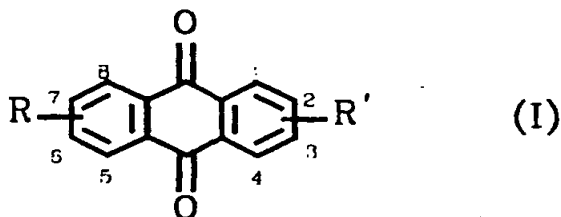
(56) Documents Cited
EP 0295676 A2 EP 0053937 A1 JP 030068623 A
US 4102873 A
J.Polym.Sci., Polym.Chem.Ed.(1985),23(11), 2779-90,
Frazer

(58) Field of Search
UK CL (Edition Q) C3R RSM
INT CL⁶ C08G 73/00 73/02
ONLINE - WPI, EPODOC, PAJ, CAS ONLINE

(54) Abstract Title
Polymers of diaminoanthracene and anthraquinone

(57) There are disclosed polymeric or oligomeric product obtainable from the reaction of an anthraquinone with an aromatic diamine, characterised in that the anthraquinone is substituted or is not substituted and in that the diamine is a diamino anthracene which is substituted or is not substituted.

The anthraquinone may be of the general formula (I):



where, R may be the same as or different to R', and may be a hydrogen atom (when R = R' = H, the compound is anthraquinone), or CH₃, CH₃CH₂-, -OCH₃, -OCH₂CH₃, -CH₂OCH₃, -CH₂OCH₂CH₂OCH₃, methoxyethoxyethoxymethyl, aryloxyethyl, phenyl, Cl, Br, CN or NO₂, -CH₂COOR or -CH₂NHCOR'' (where R'' is C₁ - C₆ alkyl or a phenyl or biphenyl group).

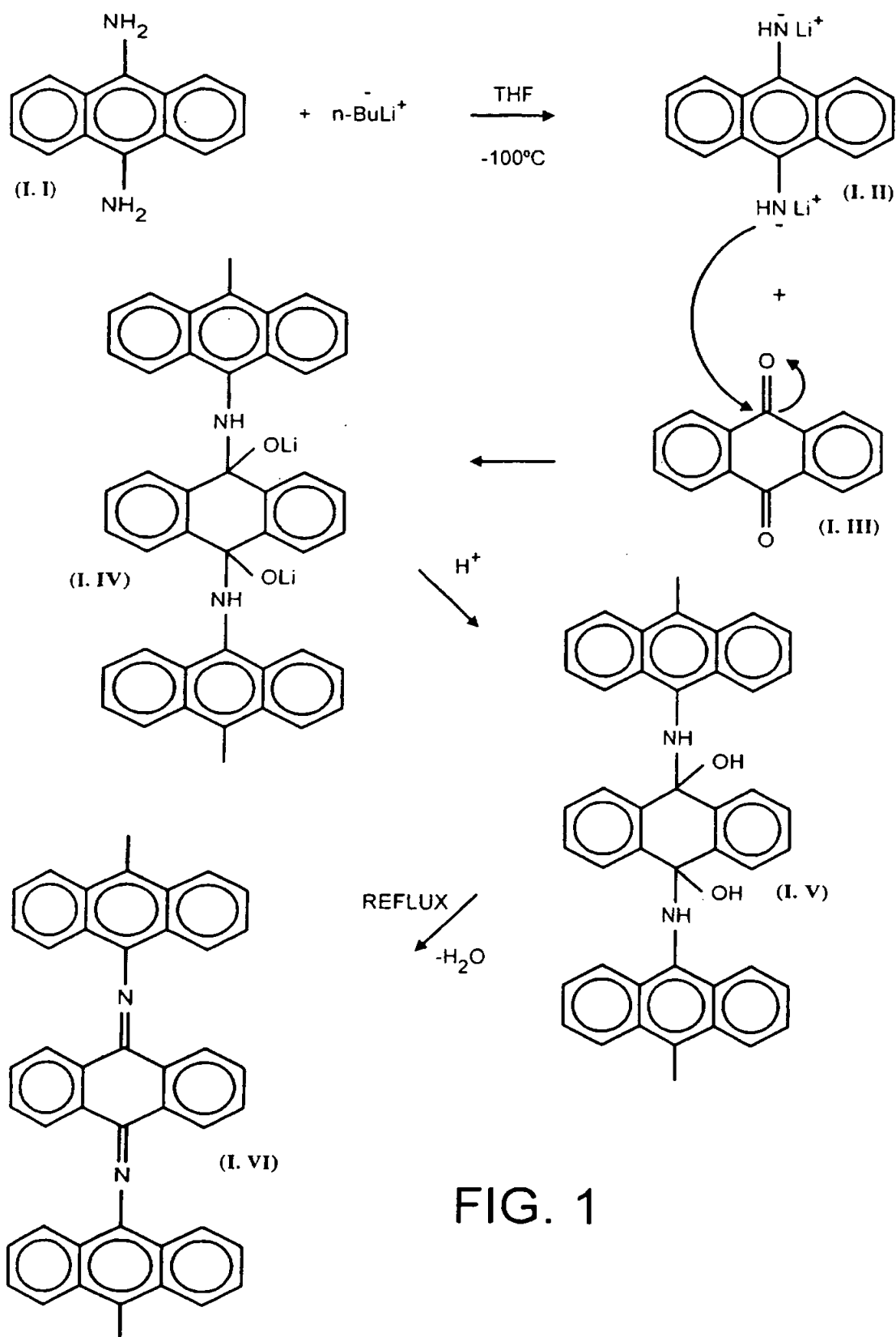


FIG. 1

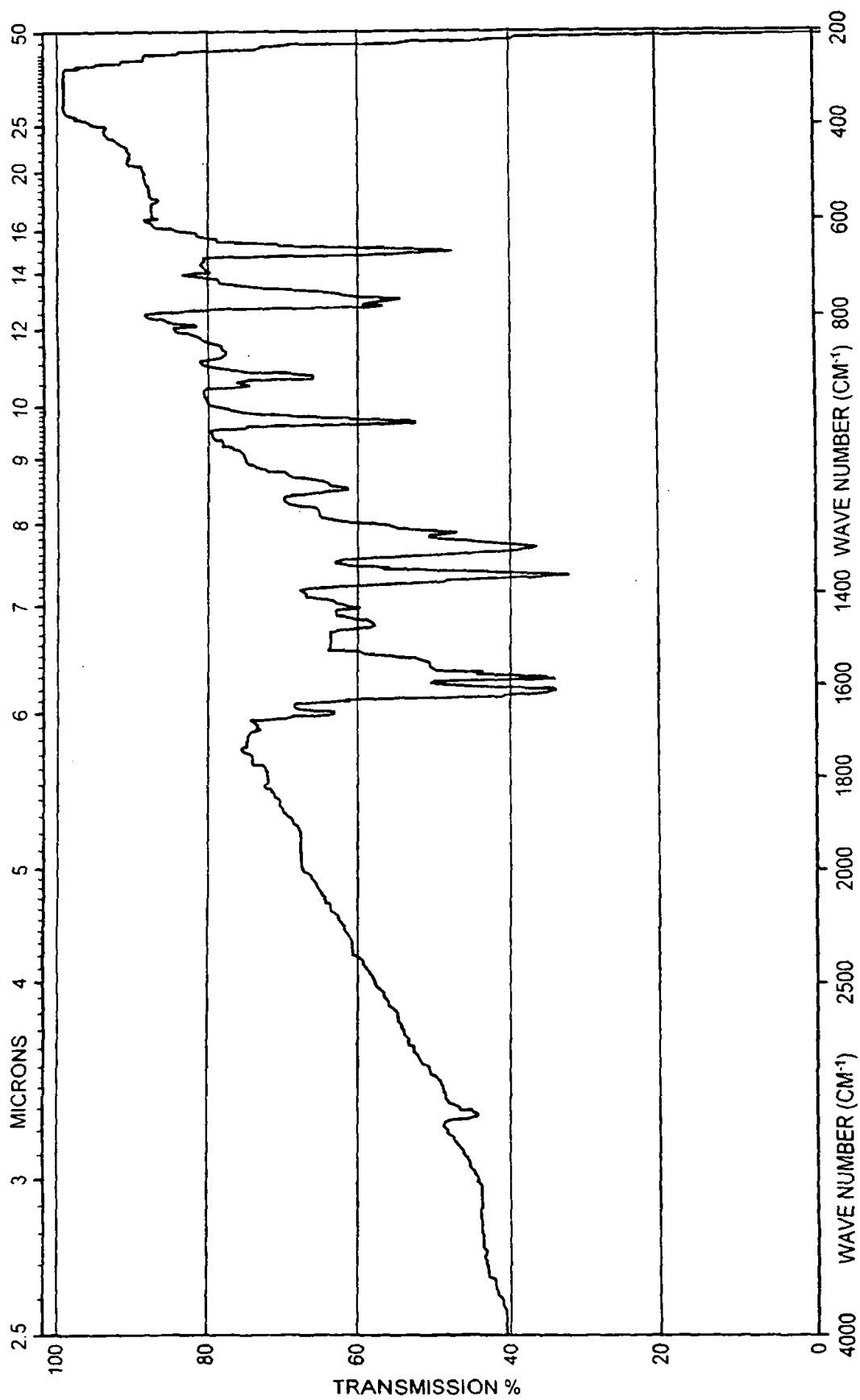


FIG. 2

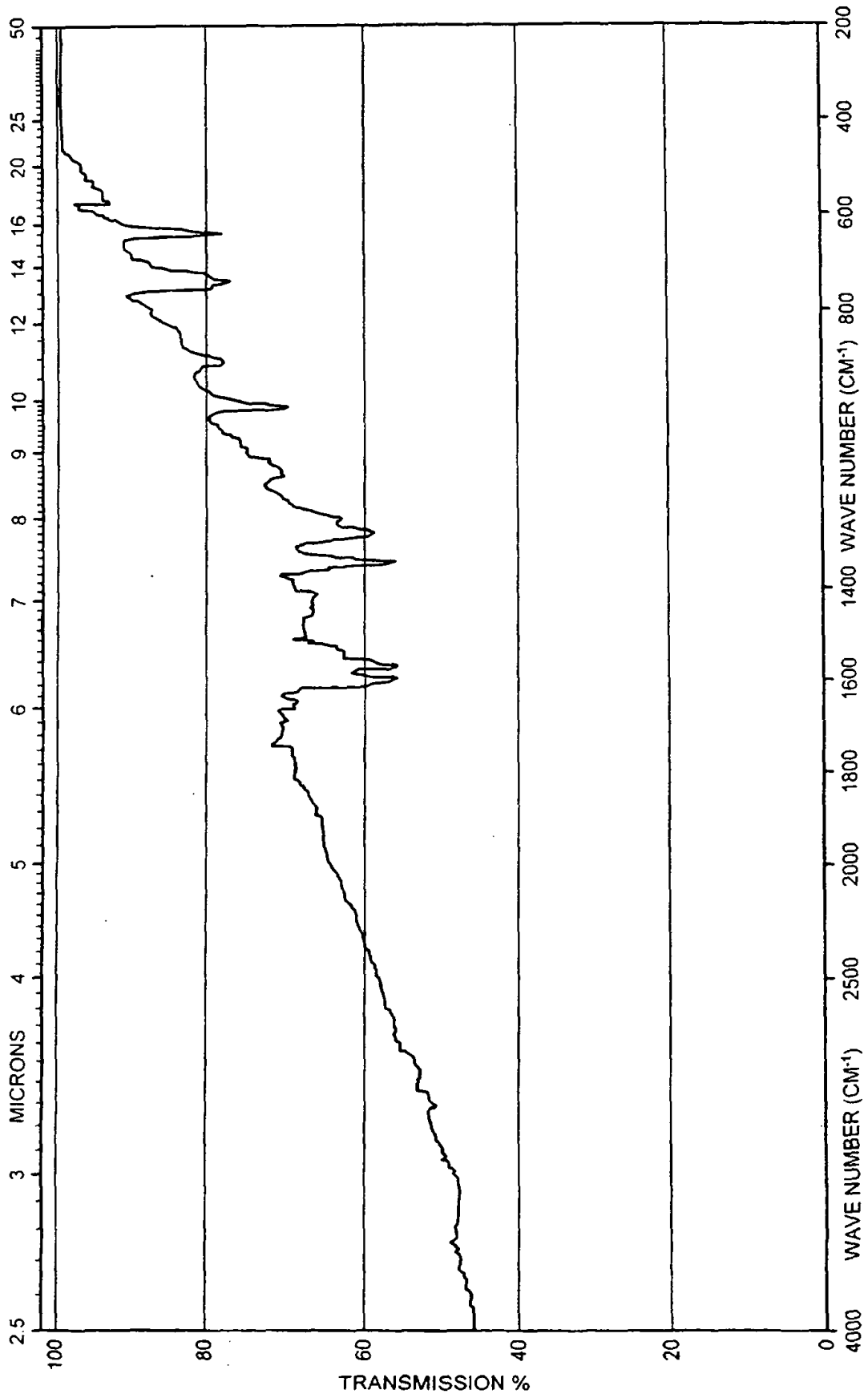
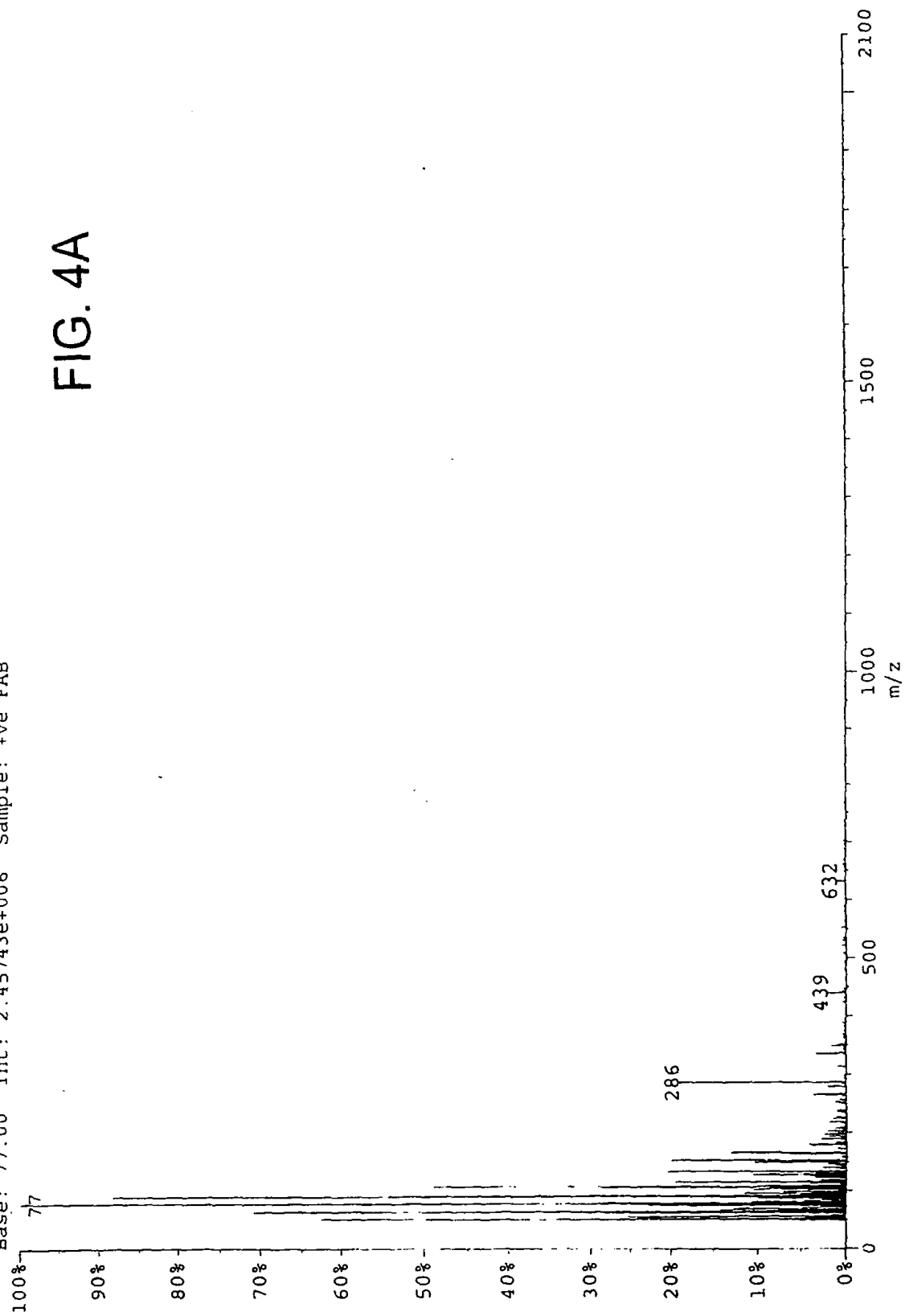
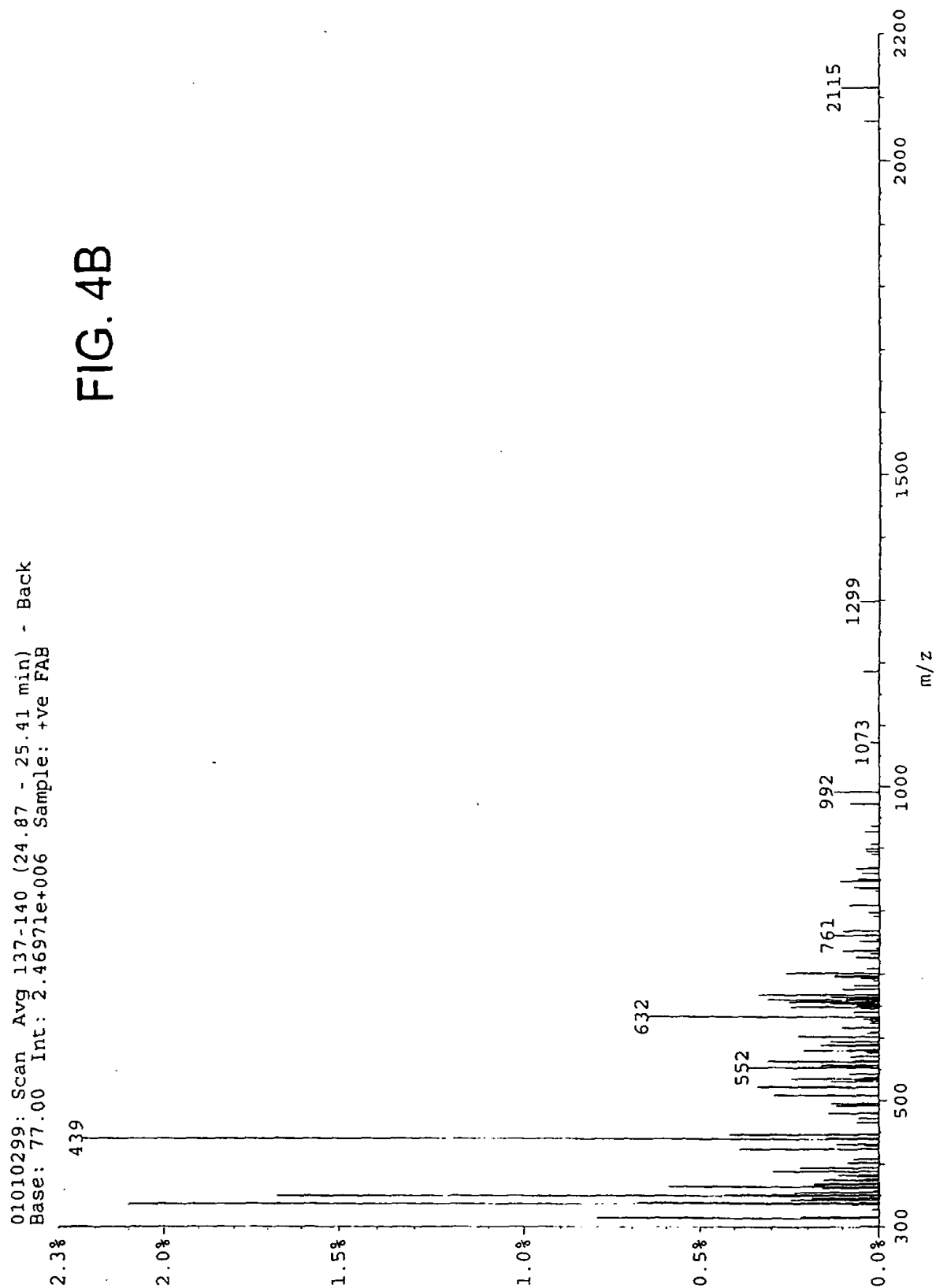


FIG. 3

01010299: Scan Avg 137-139 (24.87 - 25.23 min) - Back
Base: 77.00 Int: 2.45743e+006 Sample: +ve FAB

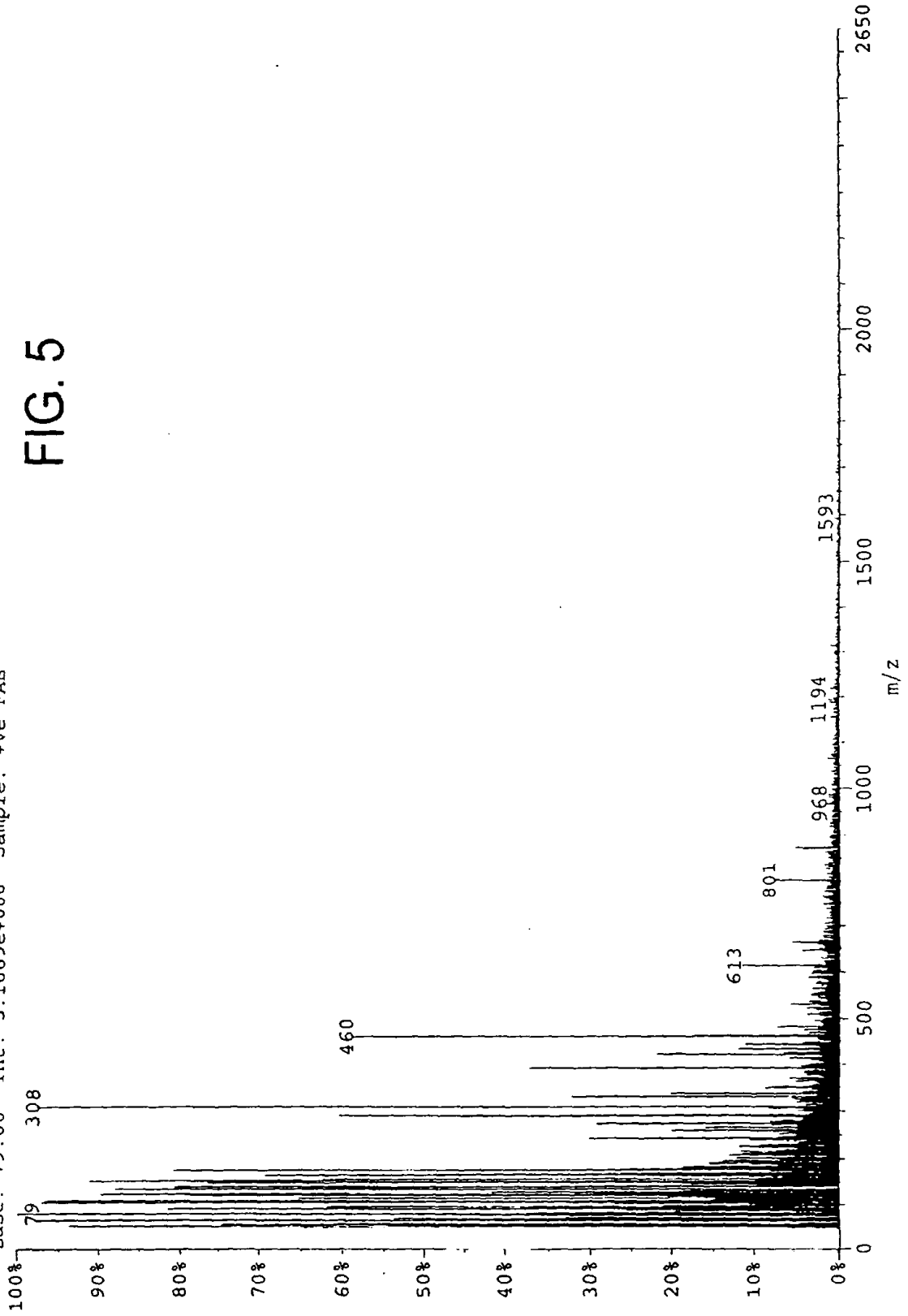
FIG. 4A





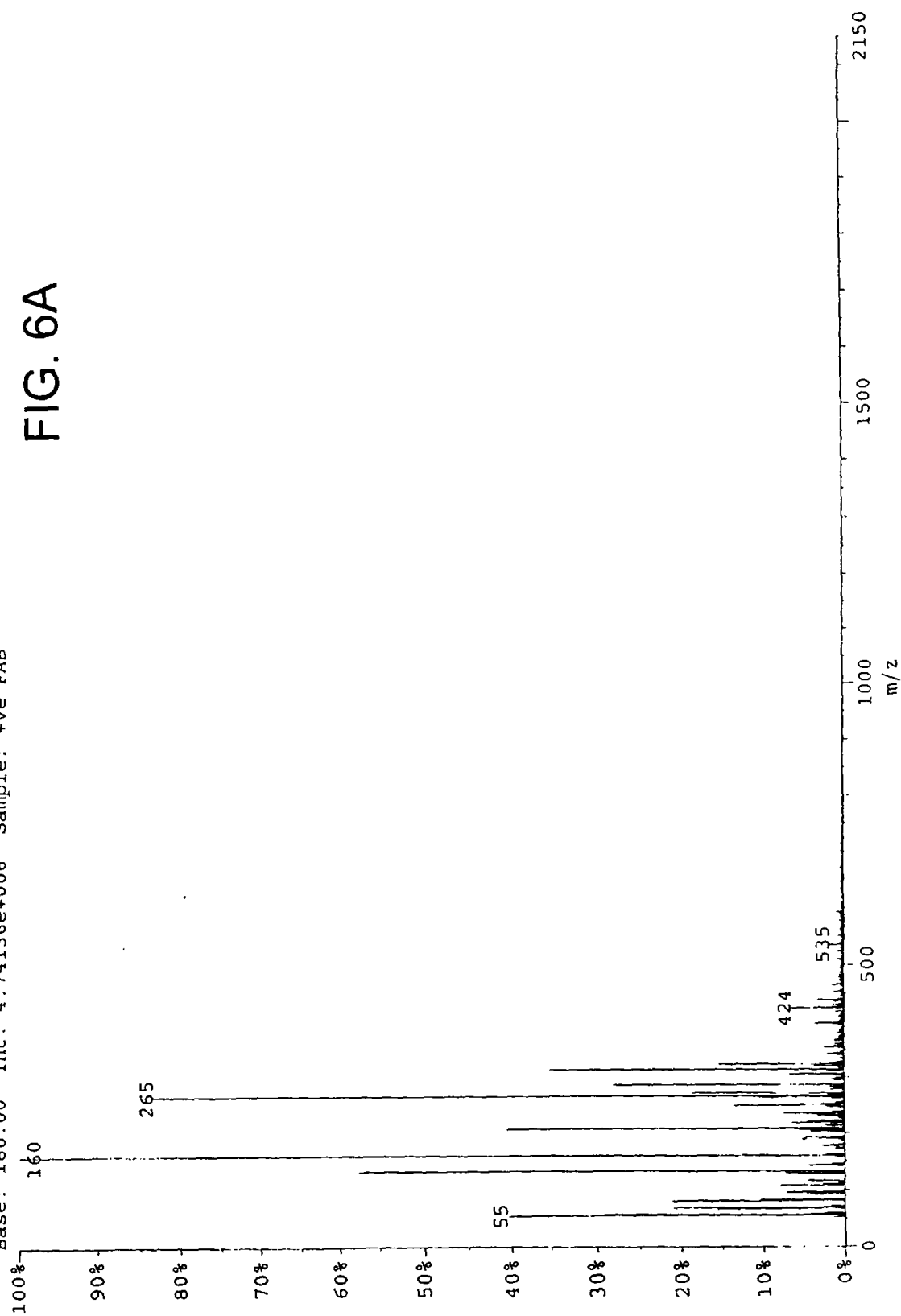
01010299: Scan 207 (37.62 min) - Back
Base: 79.00 Int: 5.1669e+006 Sample: +ve FAB

FIG. 5

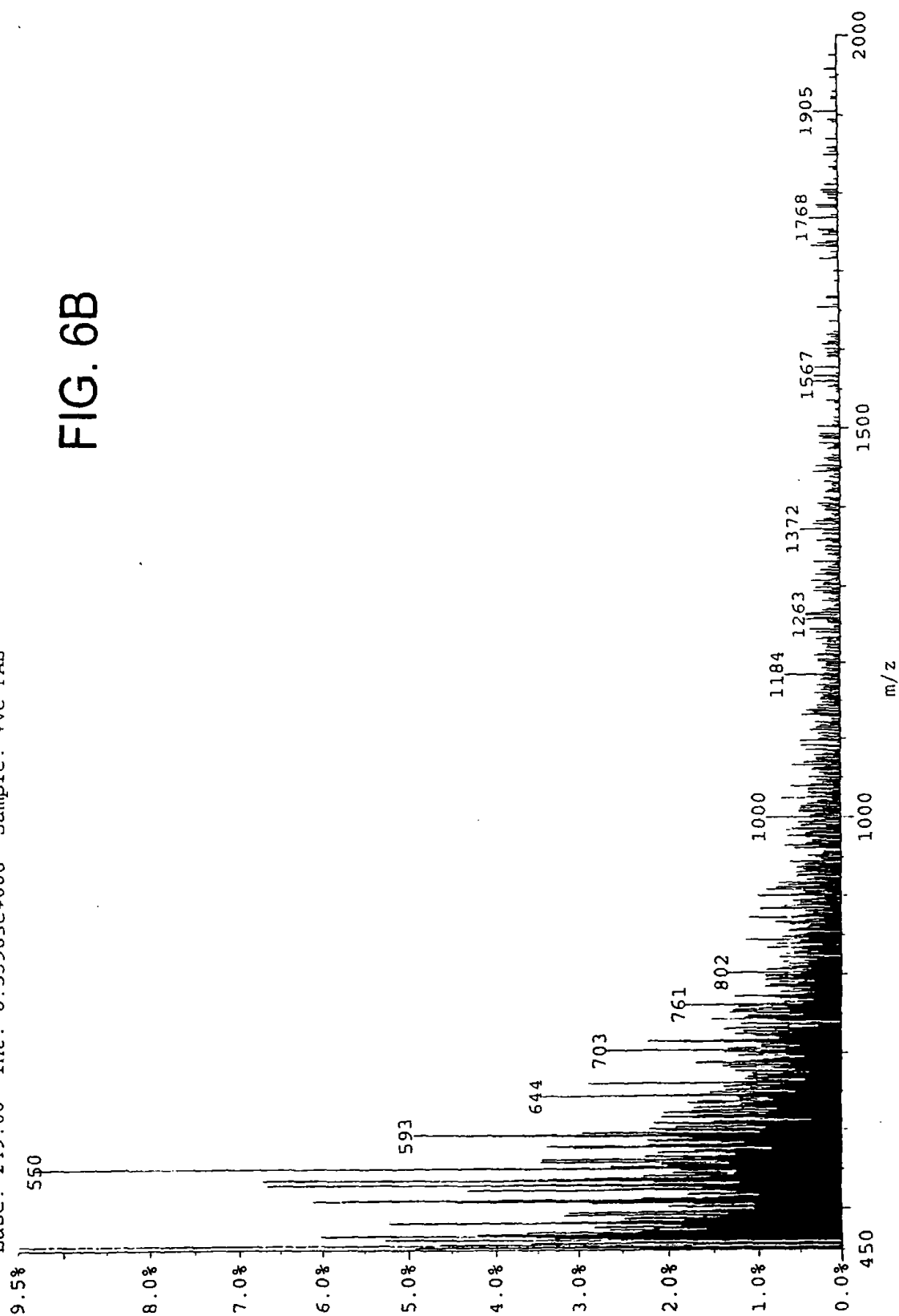


01010299: Scan Avg 322-325 (58.57 - 59.12 min) - Back
Base: 160.00 Int: 4.74136e+006 Sample: +ve FAB

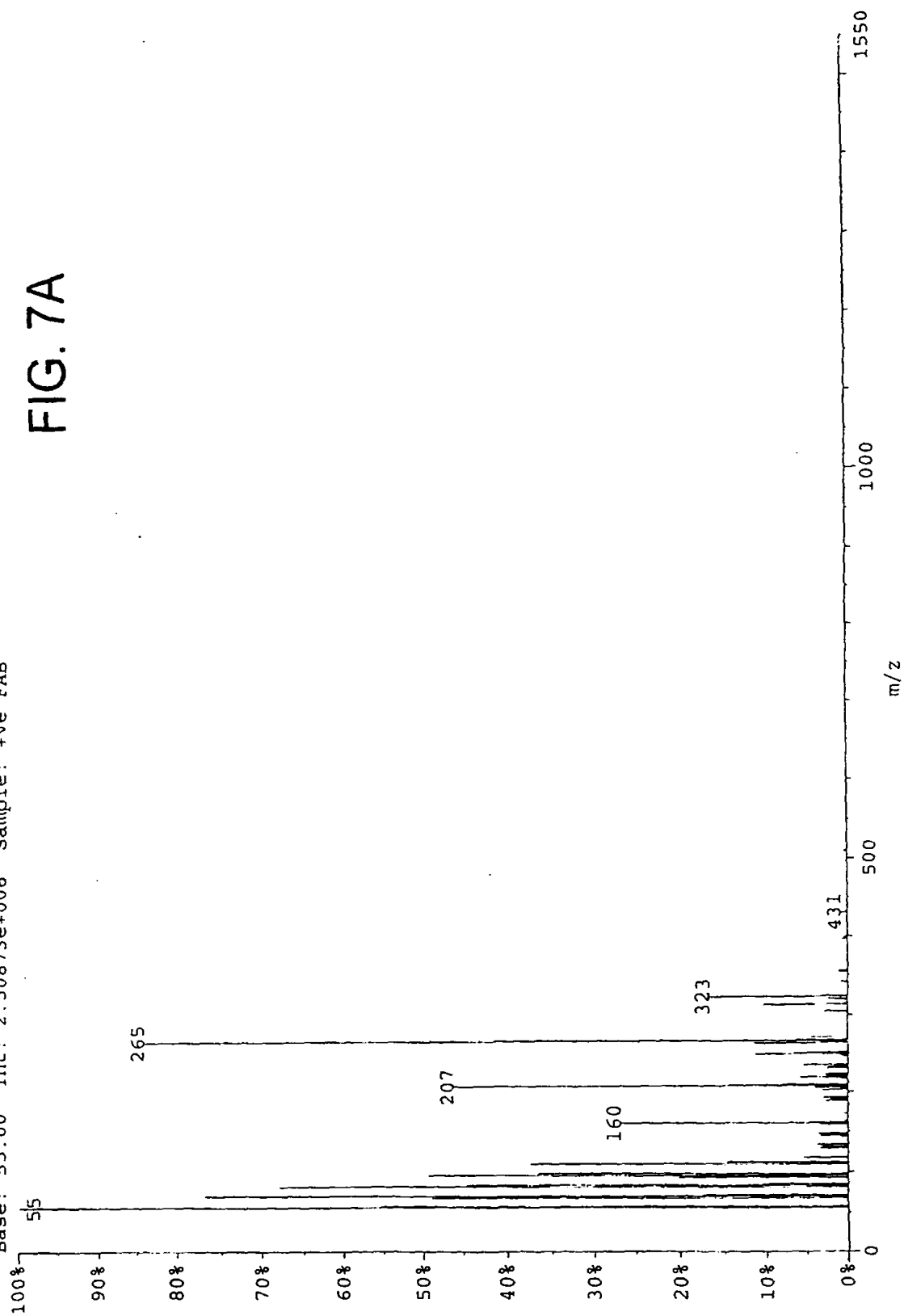
FIG. 6A



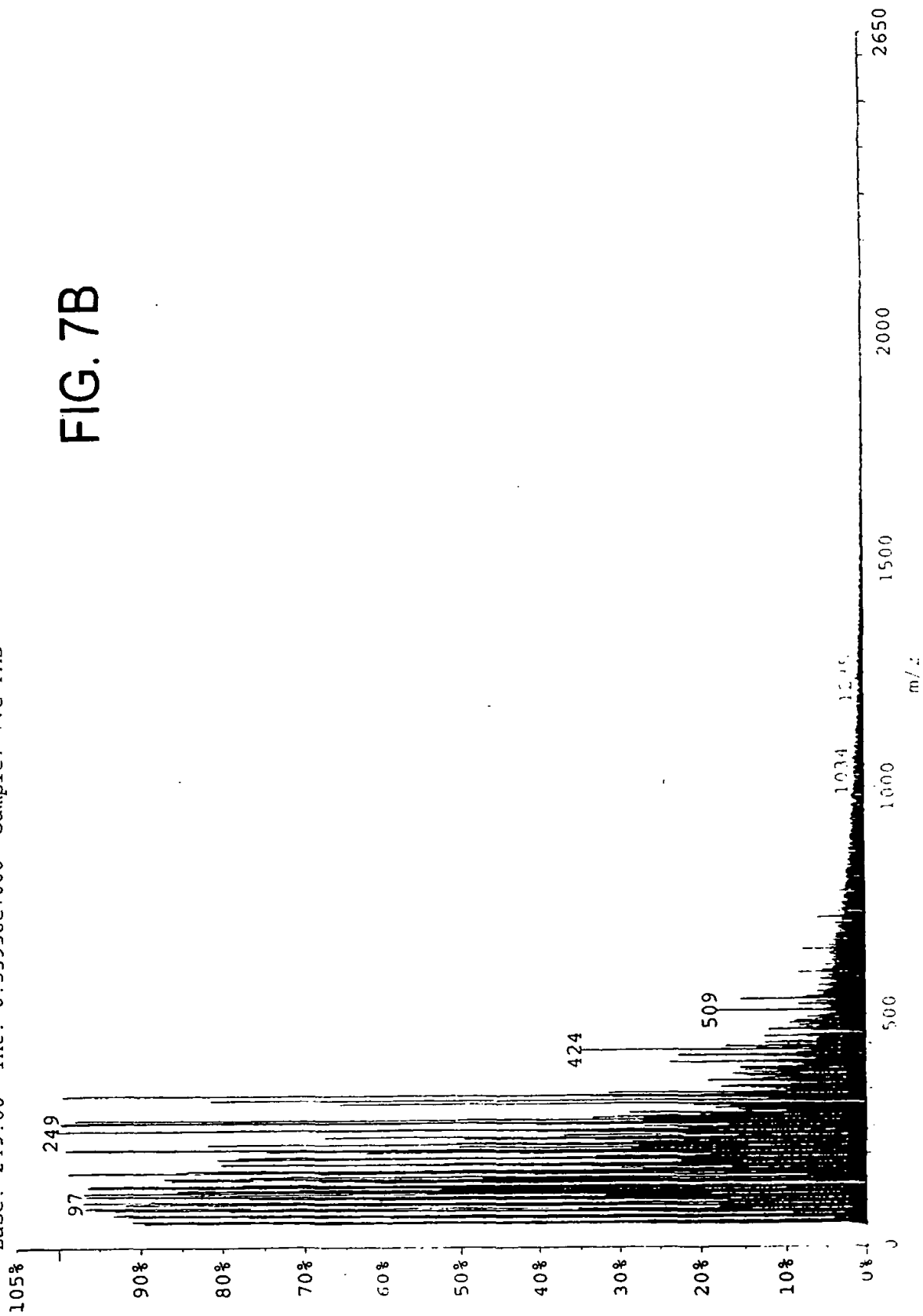
01010299: Scan 330 (60.03 min) - Back
Base: 249.00 Int: 6.53963e+006 Sample: +ve FAB



01010299: Scan Avg 38-40 (6.83 - 7.19 min) - Back
Base: 55.00 Int: 2.50873e+006 Sample: +ve FAB



01010299: Scan Avg 63-65 (11.38 - 11.75 min) - Back
Base: 249.00 Int: 6.53938e+006 Sample: +ve FAB



01180399: Scan 2312 (412.51 min) - Back
 Base: 160.00 Int: 6.5535e+006 Sample: +ve FAB

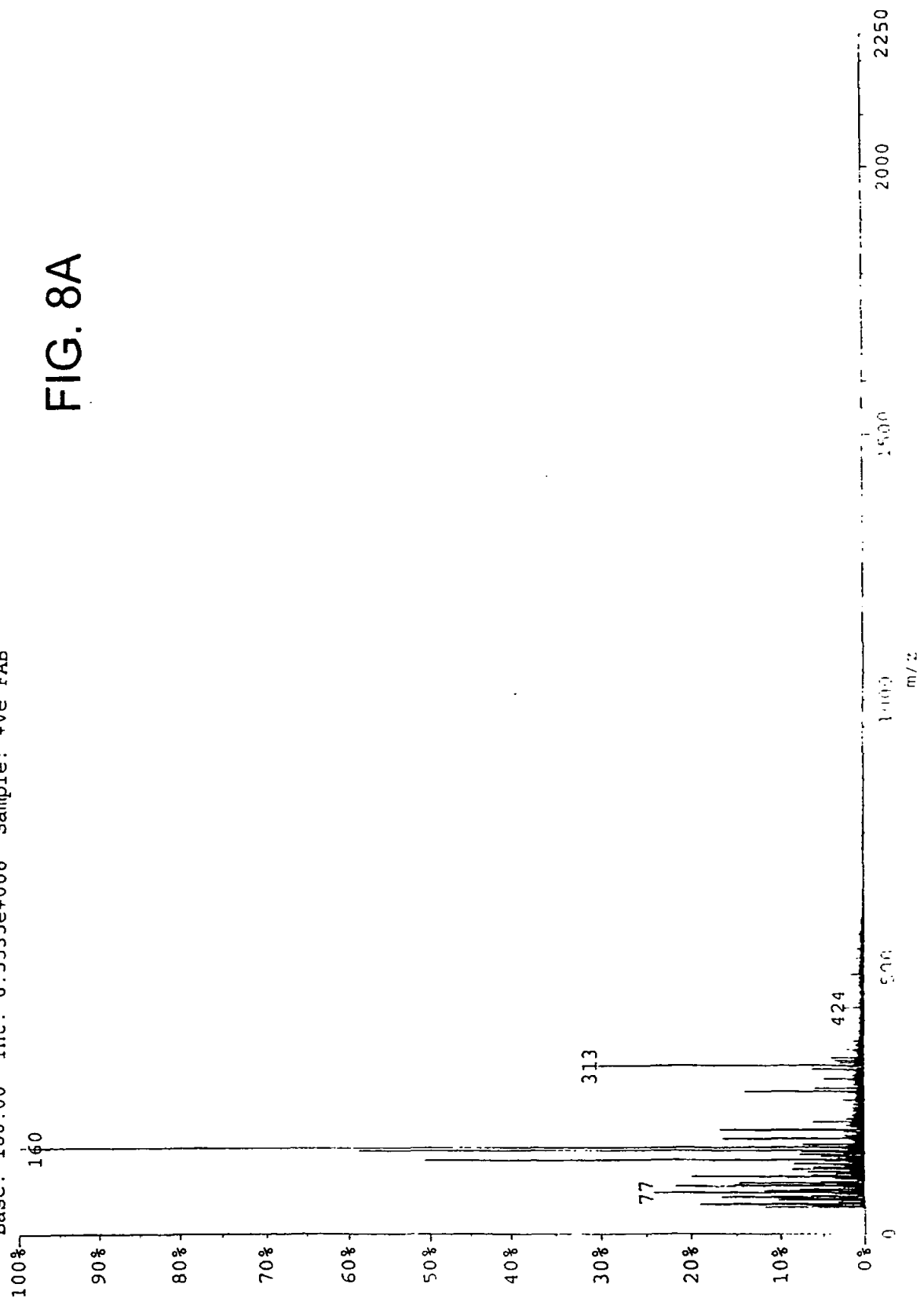


FIG. 8A

01180399: Scan Avg 2302-2307 (410.73 - 411.62 min) - Back
Base: 50.00 Int: 6.5535e+006 Sample: +ve FAB

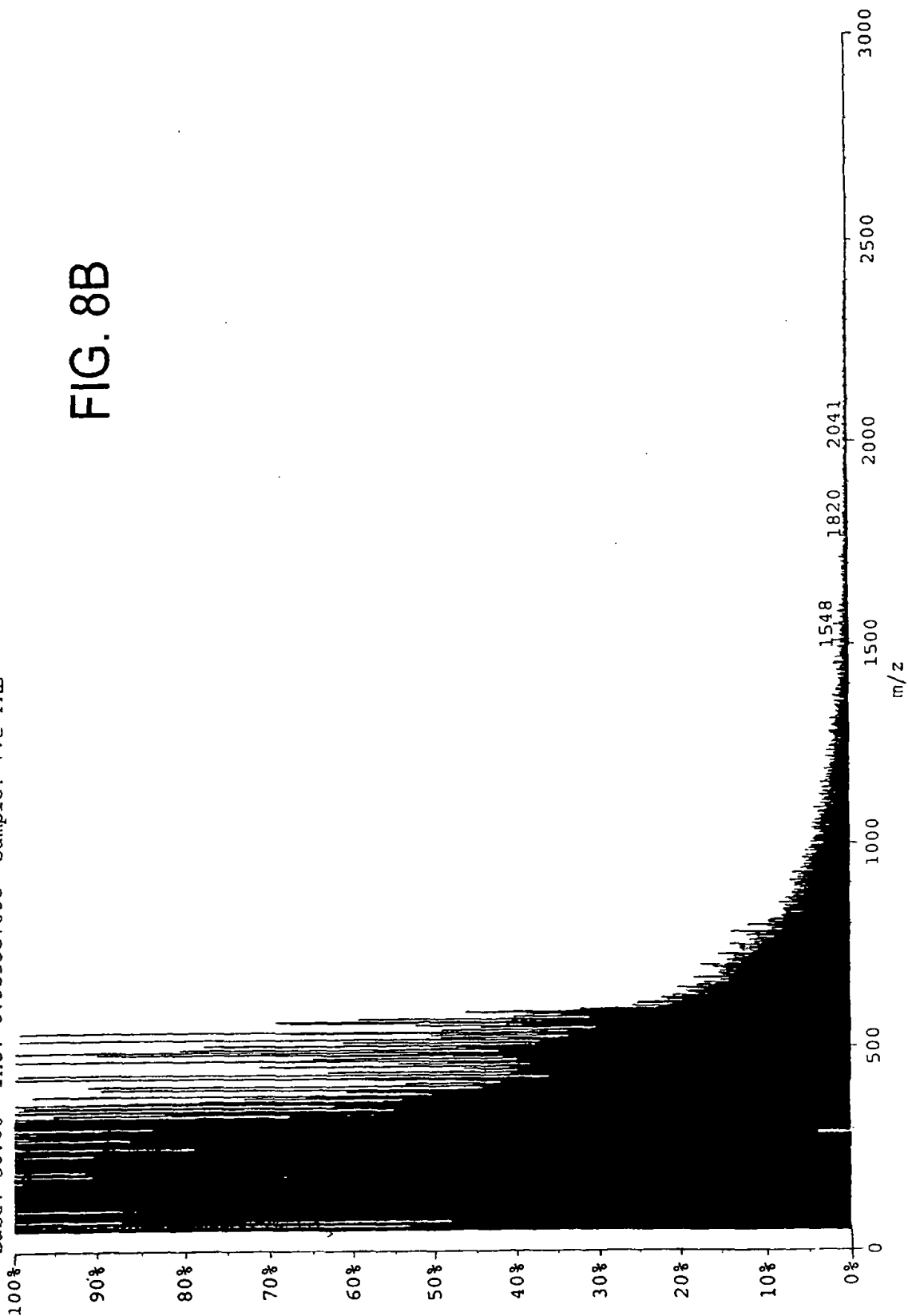
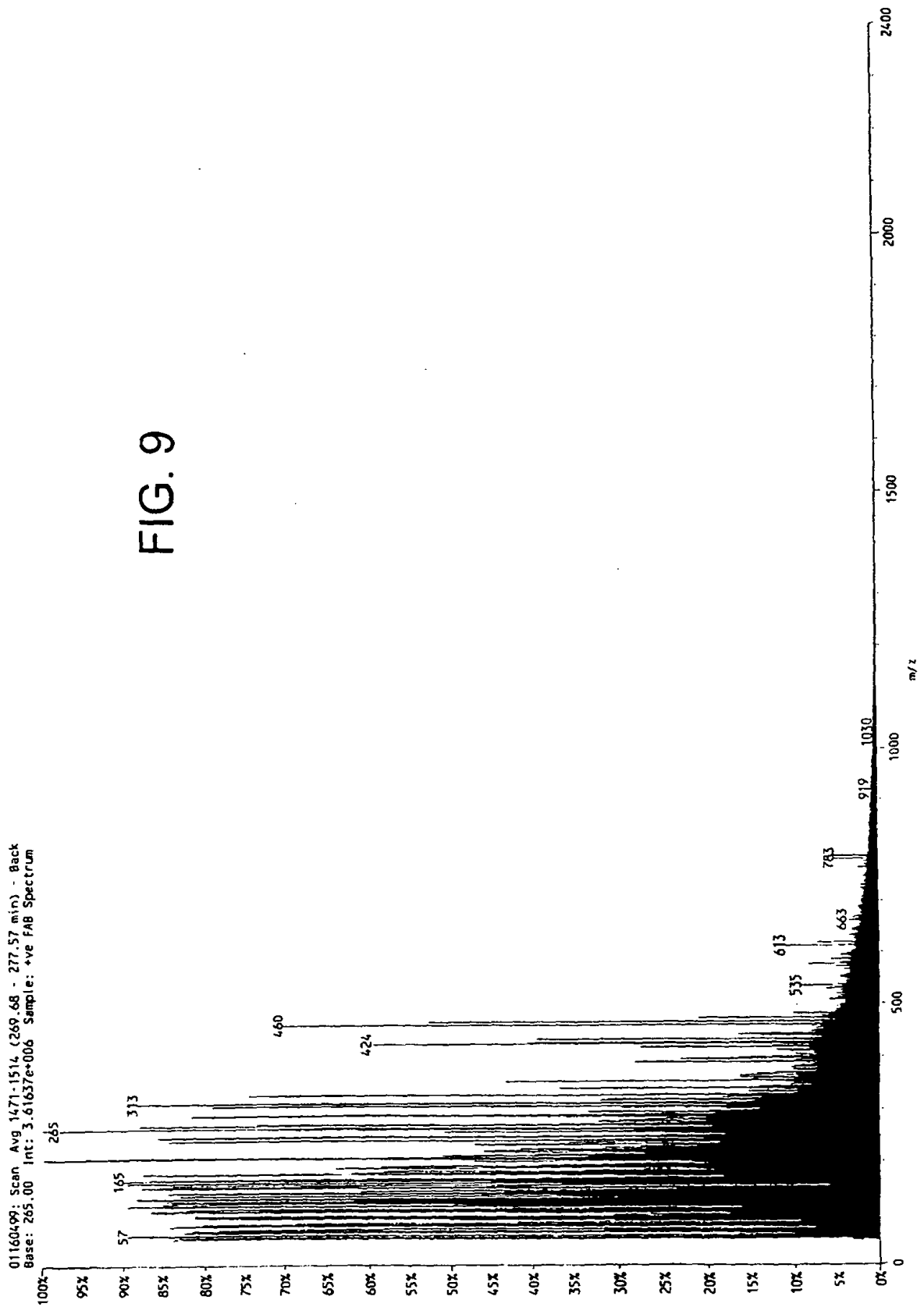


FIG. 9



POLYMERS

The present invention relates to polymerisation products of anthraquinone (AQ) with diamino anthracenes (DAA) and to their production. In particular, the invention relates to homopolymers or co-polymers of anthraquinone with 9,10 diaminoanthracene. The polymerisation products may be polymers or oligomers (e.g. of 2 to 12 or 15 repeat units) and the processes of the present invention enables homopolymers and co-polymers to be made which differ only in the substituents which are attached to the anthracene backbone. The co-polymers can be expected on reduction to produce materials which are electroconductive and fairly soluble in a range of commercially viable and environmentally friendly organic solvents. They may also be sufficiently transparent to be used in thin film applications where they may be used as transparent coatings, used extensively in displays, e.g. electroluminescent and liquid crystal displays and to some extent in electromagnetic shielding windows. The copolymers disclosed herein can be used in antistatic applications.

Polymers of aniline and applications thereof have been known for many years. Poly (1-aminoanthracene) (P1-AA hereafter) has also been described recently (Takakazu Yamamoto *et al.*, Macromolecules, 1993, 26, pages 6992 - 6997). These polymers have similar structures to poly(aniline) and are dark coloured, varying from bluish-black, brown to brown-black powders. Yamamoto states P1-AA has conductivity of the order of $1 \times 10^{-4} \text{ S cm}^{-1}$. P1-AA is stated by Yamamoto to be soluble in organic solvents such as HCOOH, DMF, DMSO and NMP, slightly soluble in CHCl_3 and THF, and insoluble in CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3CN , benzene and toluene. Yamamoto gives no indication of the transparency of P1-AA. The applicants are also aware of two articles namely A. Everaerts *et al.*, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 24 (7) pp 1703-16 (1986)(hereafter Everaerts) and P.A. Williams *et al.*, Macromolecules 26 (21) pp5820-1 (1993) (hereafter Williams)

The present inventors have been seeking to develop a conductive polymer of sufficient transparency to enable it to be used where light transmission as well as conductivity is required, and in addition solubility which would facilitate fabrication into useful structures, such as films, by solvent methods. In contrast to PI-AA we
5 have discovered surprisingly that certain polymerisation products of anthraquinone with 9,10 diaminoanthracene are sufficiently transparent and soluble electroconductive polymers.

These products may exhibit a particular advantage over the transparent Indium Tin Oxide (ITO) films currently employed in transparent coatings. The ITO coatings
10 lose most or all of their electroconductivity if the surface is bent. However, the products according to the present invention can be expected to maintain their electroconductivity even when bent.

In addition the present inventors wished to devise a procedure by which polymers could be provided in which the polymer backbone was constant and
15 maximum flexibility was provided for varying the substitution on the backbone.

According to one aspect of the present invention, there is provided a polymeric or oligomeric product obtainable from the reaction of an anthraquinone with an aromatic diamine, characterised in that the anthraquinone is substituted or is not substituted and in that the diamine is a diamino anthracene which is
20 substituted or is not substituted. These are preferably produced by polycondensation.

The substitution may be such that the product is a homopolymer or homooligomer, or the substitution may be such that the product is a co-polymer or a co-oligomer.
25 The diaminoanthracene is preferably a 9,10-diaminoanthracene, which may be substituted or not.

The DAA may be substituted with a single substituent e.g. a C₁ - C₅ alkyl, an aryl e.g. a benzyl group, an -SO₃H, or -OH, or C₁ - C₅ alkoxy, or aryloxy, e.g. phenoxy or substituted phenoxy or biphenyloxy group or an H₂PO₃ group or with
30 more than one substituent.

The invention also extends to products in which the anthraquinone is replaced wholly or in part by one or more substituted anthraquinones. Commercially available substituted anthraquinones include:

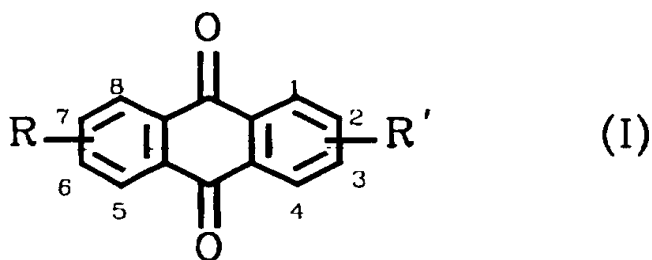
- 5 1-methylaminoanthraquinone;
- 2-aminoanthraquinone;
- 1-aminoanthraquinone;
- 9,10-Anthraquinone-2-sulphonic acid sodium salt;
- 9,10-Anthraquinone-1,5-disulphonic acid disodium salt;
- 10 1-chloroanthraquinone
- 2-Methylanthraquinone;
- 2-Ethylanthraquinone;
- 9,10-Anthraquinone-2,6-disulphonic acid disodium salt;
- 2-(Hydroxymethyl)anthraquinone;
- 15 Anthraquinone-2-carboxylic acid, (contains 98% 9,10-dihydro-9,10-dioxo-2-anthracenecarboxylic acid)
- 1,5 dihydroxyanthraquinone;
- 1,4 dihydroxyanthraquinone;
- 1,4-Bis (methylamino)anthraquinone;
- 20 Benz [a] anthracene -7,12-dione;
- 1,4-Diaminoanthraquinone;
- 1,5-Dichloroanthraquinone;
- 1,5-Dinitro-9,10-anthraquinone;
- 2,3,6,7-Tetramethyl-anthraquinone;
- 25 1-Hydroxy-4-(paratoluidine) anthraquinone;
- 1-Alkyloxy-3-methoxymethoxy-anthraquinone;
- 2,6-Di-tert-butyl-anthraquinone;
- 1-Amino-2-bromo-4-p-tolylamino-anthraquinone;
- 30 1-Hydroxy-2-pent-2-enyl-anthraquinone;
- 1-Amino-4-hydroxy-anthraquinone;
- 2-[(2-Amino-ethylamino)-methyl]-anthraquinone, dihydrobromide;

- 1,4-Dimethyl-anthraquinone;
 1,4-Diamino-2,3-bis-phenoxy-anthraquinone;
 2,7-Dimethyl-anthraquinone;
 1,2-Dimethyl-anthraquinone;
 5 1-Iodo-2-methyl-anthraquinone;

The ratio of anthraquinone to aromatic diamine is in the range preferably of 5:1 to 1:5, eg. in the range 3:1 to 1:3, more preferably in the range 2:1 to 1:2, e.g. 1:1. Preferably the anthraquinone is a $C_1 - C_6$ alkyl anthraquinone or a $C_1 - C_{10}$ alkoxy anthraquinone or a hydroxyanthraquinone, for example the anthraquinone may be 2-ethyl anthraquinone or 2-methyl anthraquinone, or 2,3-dimethyl anthraquinone or 2,6-dioctyloxy anthraquinone or 2,6-dihydroxyanthraquinone.

- The diaminoanthrance may be substituted in the same way as the anthraquinone and with the same range of substituents.
- 15 Preferred substituted anthraquinones are $C_1 - C_6$ alkyl anthraquinones e.g. 2-ethyl anthraquinone or 2-methyl anthraquinone, or 2,3-dimethyl anthraquinone or $C_1 - C_{10}$ alkoxy anthraquinones e.g. 2,6-dioctyloxy anthraquinone or hydroxyanthraquinones e.g. 2,6-dihydroxyanthraquinone.

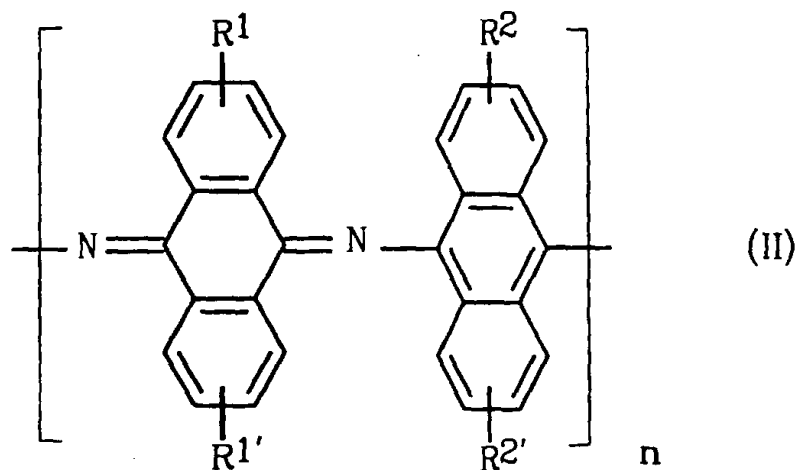
20 More broadly, the substituted anthraquinones may be of general formula (I):



- where, R may be the same as or different to R' , and may be a hydrogen atom (when $R = R' = H$, the compound is anthraquinone), or CH_3 , CH_3CH_2- , $-OCH_3$, $-OCH_2CH_3$, $-CH_2OCH_3$, $-CH_2OCH_2CH_2OCH_3$, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, CN or NO_2 , $-CH_2COOR$ or $-CH_2NHCOR''$ (where R'' is $C_1 - C_6$ alkyl or a phenyl or biphenyl group).

The invention also extends to polymeric products having the general formula

(II)

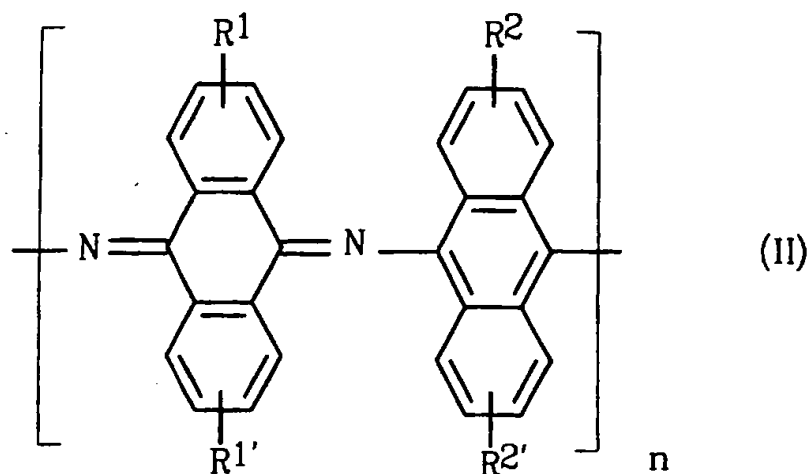


5

where, R^1 may be the same as or different to R' , which may be the same as or different to R^2 , which may be the same as or different to $R^{2'}$, and each of $R^1, R^{1'}, R^2$ and $R^{2'}$ may be a hydrogen atom or CH_3 , CH_3CH_2- , $-OCH_3$, $-OCH_2CH_3$, $-CH_2OCH_3$, $-CH_2OCH_2CH_2OCH_3$, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, CN or NO_2 , $-CH_2COOR$ or $-CH_2NHCOR'''$ (where R''' is $C_1 - C_6$ alkyl or a phenyl or biphenyl group), or a $C_1 - C_5$ alkyl group, or an aryl group e.g. a benzyl group, or an $-SO_3H$ group or a hydroxyl group or a $C_1 - C_5$ alkoxy group or an H_2PO_3 group, and R^1 and $R^{1'}$ are different to R^2 and $R^{2'}$ and n is an integer ranging from 2 to 100 preferably from 10 to 100, preferably 50 to 80, e.g. about 70.

10

The invention also extends to polymeric products having the general formula (II)



5 where, R^1 may be the same as or different to $R^{1'}$, and each of R^1 and $R^{1'}$ is a hydrogen atom or CH_3 , CH_3CH_2 , $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl , CN or NO_2 , $-\text{CH}_2\text{COOR}$ or $-\text{CH}_2\text{NHCOR}'''$ (where R''' is $\text{C}_1 - \text{C}_6$ alkyl or a phenyl or biphenyl group), and R^2 may be the same or different to $R^{2'}$ and each of R^2 and $R^{2'}$ is a hydrogen atom or a $\text{C}_1 - \text{C}_5$ alkyl group, or an aryl group e.g. a benzyl group, or an $-\text{SO}_3\text{H}$ group or a hydroxyl group or a $\text{C}_1 - \text{C}_5$ alkoxy group or an H_2PO_3 group, and R^1 and $R^{1'}$ are different to R^2 and $R^{2'}$ and n is an integer ranging from 2 to 100 preferably from 10 to 100.

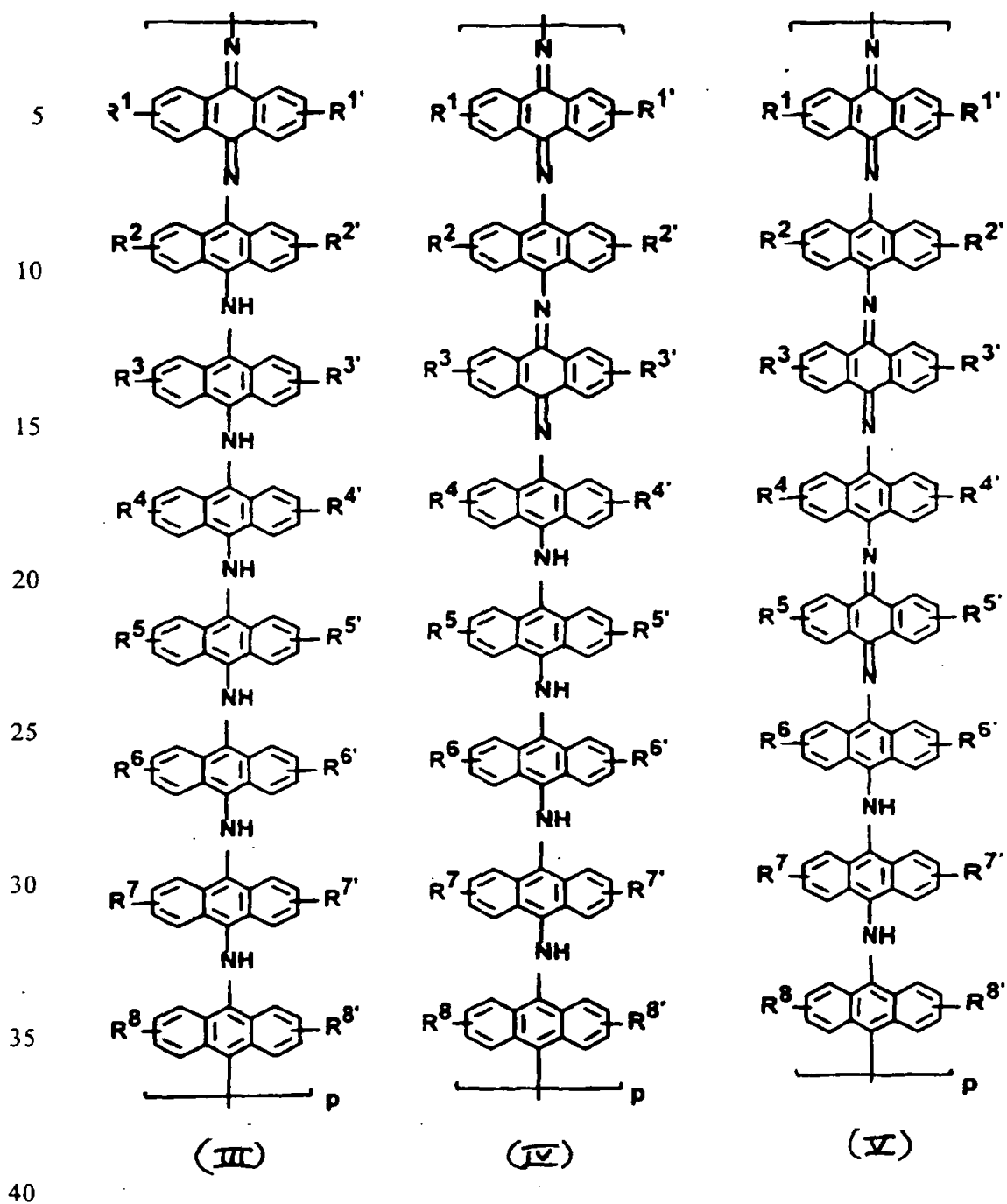
15 In one form of the invention R^1 is the same as $R^{1'}$ but is different from R^2 and $R^{2'}$ and in that R^2 and $R^{2'}$ are the same, i.e. a copolymeric form.

In another form of the invention R^1 is the same as $R^{1'}$ and as R^2 and $R^{2'}$ but is not hydrogen, i.e. a homopolymeric form.

20 In another form of the invention R^1 is different from $R^{1'}$ and R^2 is different from $R^{2'}$ and R^1 and $R^{1'}$ are both different from R^2 and $R^{2'}$, i.e. a copolymeric form.

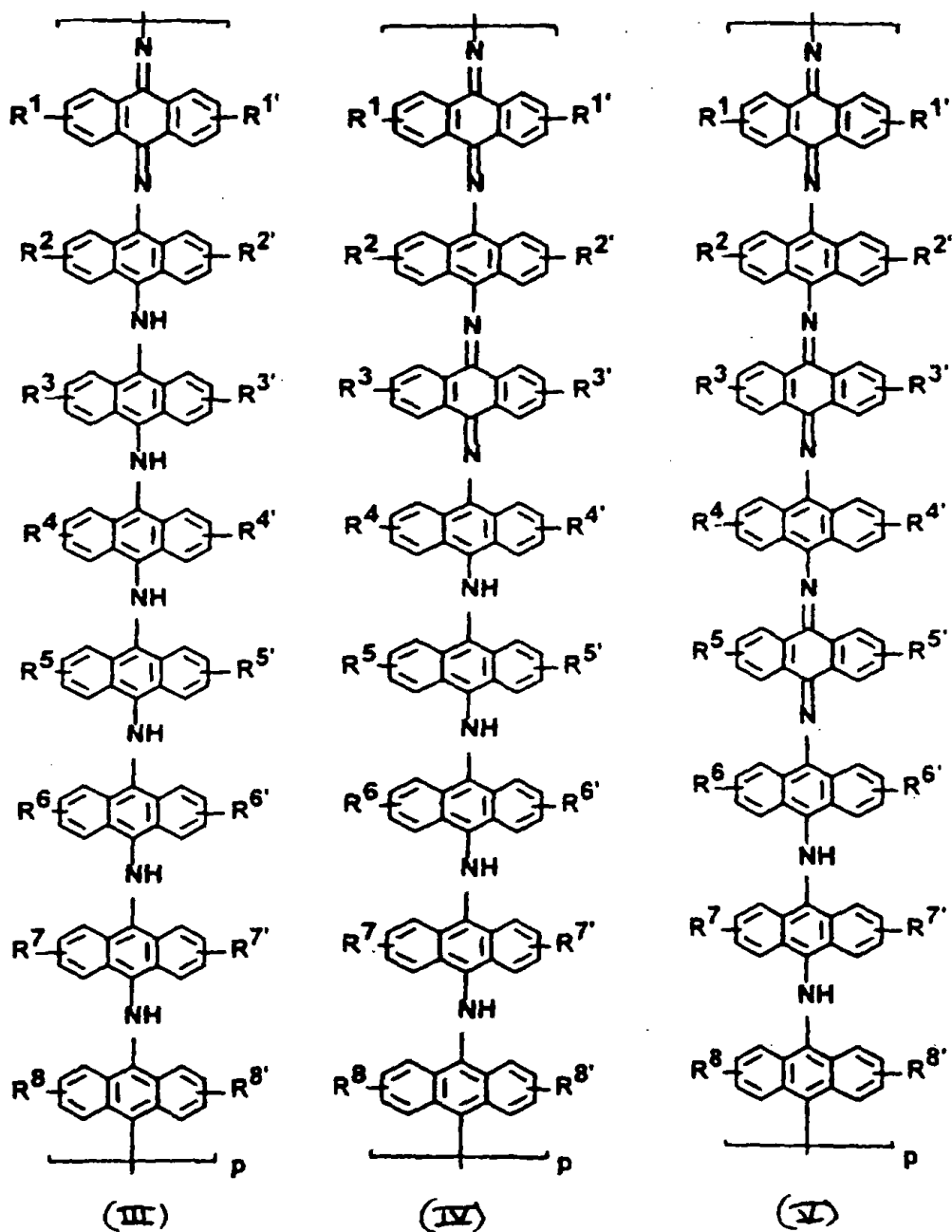
In another form of the invention R^1 and R^2 are not hydrogen and $R^{1'}$ and $R^{2'}$ are not the same, i.e. a copolymeric form.

Poly (9-aminoanthracene)s in accordance with the invention are also provided characterised in that they have an oxidation state between 0.25 to 0.75,
5 and a formula (III) at an oxidation state 0.25, a formula (IV) at an oxidation state 0.5 and a formula (V) at an oxidation state 0.75 as follows



in which R^1 to R^8 are not all hydrogen.

Poly (9-aminoanthracenes) in accordance with the invention are also provided characterised in that they have an oxidation state between 0.25 to 0.75, and a formula (III) at an oxidation state 0.25 , a formula (IV) at an oxidation state 0.5 and a formula (V) at an oxidation state 0.75 as follows



in which the R groups are the same as the R' groups and the R groups are all the same;

or

5 the R groups are the same as the R' groups and the R¹, R³, R⁵ and R⁷ groups are all the same and the R², R⁴, R⁶ and R⁸ groups are all the same but are different to the R¹, R³, R⁵ and R⁷ groups;

or

10 the R groups are different to the R' groups and the R¹, R³, R⁵ and R⁷ groups are all the same and the R², R⁴, R⁶ and R⁸ groups are all the same but are different to the R¹, R³, R⁵ and R⁷ groups.

Polymers with lower values of p, e.g. 2 to 10, or 2-15 which may be referred to as oligomers, will have higher solubility but may have lower heat stability.

15 The co-polymers of the invention can be expected on reduction to produce materials which are conductive and therefore may find uses in thin film technology, as EMI, RFI (electro magnetic interference, radio frequency interference) shielding materials and in display systems, such as electroluminescent and liquid crystal display systems as a transparent electrode.

The copolymers disclosed herein can be used even without reduction in antistatic applications.

20 Such reduced polymeric products may be used with other polymers (or binders). The polymeric product - binder blend may comprise from 5 to 70 % by weight of the polymeric product and from 95 to 30 % by weight of the other polymer. The polymer with which the polymeric product is blended may be, for example, poly(vinyl chloride), polyethylene, polypropylene, polystyrene, nylon, 25 poly(acrylonitrile-butadiene-styrene), poly(ethylene terephthalate), poly(ethylene oxide), polymethyl methacrylate, polyether sulphone, polyether ketone, polytetrafluoroethylene.

30 These blends may have sufficient conductivities to give good antistatic properties at the lower concentrations of polymeric product. At the higher concentrations the blends may possess levels of conductivity which may be useful for shielding.

Furthermore, the polymeric product imparts the required electrical property to the blend immediately and unlike alkylammonium salts, do not need moisture to impart conductivity to the polymer.

Conductive adhesives may be formulated using the polymeric product of the present invention.

The polymeric product of the present invention may also be directly deposited chemically or electrochemically onto and/or impregnated into a porous polymer film such as poly(vinyl chloride), poly(carbonate) or poly(propylene). The surface of a component so formed can be permanently conductive and may have good antistatic properties.

This surface may be painted with coloured dyes or pigments and the colour modified without impairing the antistatic properties. This method may enable antistatic floors and mats to be fabricated from the composites.

Furthermore, non-conductive materials such as talc or mica may be coated with the polymeric product of the invention either chemically or electrochemically. Such coated powders may be useful as fillers for the formation of conductive polymer composites.

Furthermore, solutions of the solvent soluble polymeric product may be sprayed onto a non-conducting surface which can then become conductive on evaporation of the solvent therefrom. The resulting film can be used in display devices.

The invention also extends to a method of production of a homopolymer or copolymer or homo-oligomer or co-oligomer product characterised in that the product is obtained by condensation of an anthraquinone, substituted or not with a diaminoanthracene, substituted or not. Thus the polymeric product of the present invention may be prepared by the polycondensation of anthraquinone with DAA e.g. 9,10 diaminoanthracene using a titanium compound as a condensing agent. Examples of suitable titanium compounds include titanium tetrachloride and titanium alkoxides such as titanium tetraisopropoxide and titanium tetra-n-butoxide. Typically, a hindered base is also present in the reaction. Examples of such bases include 1,4-diazabicyclo[2,2,2] octane (Dabco), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and

quinuclidine. Lewis acids, such as molybdenum pentachloride, aluminium chloride and ruthenium trichloride, may also be employed.

Preferably the diamino anthracene is dissolved in a suitable solvent and is heated with the titanium compound and a hindered base, the anthraquinone compound is added to the mixture and the mixture is stirred and heated e.g. for a period in excess of 12 hours, the mixture is filtered and the residue is washed and the product is purified.

Preferably the ratio of anthraquinone to DAA is in the range 5:1 to 1:5, more preferably in the range 3:1 to 1:3 and most preferably in the range 2:1 to 1:2, e.g. 1:1.

An alternative reaction procedure is merely to heat the anthraquinone and the DAA together e.g. in the presence of a solvent but in the absence of a catalyst or any other species e.g. used to facilitate condensation. This produces purer species but at lower yields as compared to catalysed reaction systems.

If substituted anthraquinones are used then low yields can be tolerated because one can recover unreacted substituted anthraquinones and moreover DAA by differential solubilisation using different solvents to dissolve out these soluble species e.g. sequentially.

The polymeric products produced may be dissolved in common organic solvents such as chloroform, or tetrahydrofuran and may also be processable into thin films. It is also possible to partially reduce the produced polymeric products with a suitable reducing agent, for example sodium cyanoborohydride, sodium borohydride, sodium borohydride-boron trifluoride etherate, lithium aluminium hydride, hydrazine and dithionites. These partially reduced polymeric products may have a lighter colour and sufficient electroconductivity to be used in transparent thin film technology. It is also possible to dope these polymeric products with suitable acid dopants, for example camphorsulphonic acid, 5-sulphosalicylic acid, para-toluenesulphonic acid, trifluoromethanesulphonic acid (triflic acid), methanesulphonic acid, trifluoroacetic acid, hydrochloric acid and sulphuric acid. This may enhance the electroconductivity of the polymeric product.

The invention also extends to a transparent electroconductive coating or to a static shielding material comprising a product in accordance with the present invention.

The invention also extends to a process which comprises reacting a lithium salt of DAA substituted or not with an anthraquinone substituted or not. In a preferred form of this aspect the invention also extends to a method in which DAA substituted or not is reacted in a solvent under inert gas with an organolithium compound, e.g. n-butyllithium or lithium diisopropyl amide, at low temperature, at which the resulting lithium DAA salt is stable, preferably -70°C or lower, but above the freezing point of the reaction mixture, to produce a DAA lithium salt, the temperature of the reaction mixture is then allowed to rise e.g. to at least -20°C, preferably to room temperature and the reaction mixture is then added to anthraquinone, substituted or not, and the reaction allowed to occur, preferably at elevated temperature, e.g. by refluxing, to remove the water produced in the condensation reaction from the reaction mixture.

Lithium diisopropylamide may be used instead of butyllithium because it has the advantage of being a hindered compound as compared to butyl lithium and thus may be expected to have a lesser tendency to react with the carbonyl group of the anthraquinone. If desired the reaction solvent e.g. tetrahydrofuran can be replaced by a higher boiling solvent e.g. diglyme. Preferably such replacement solvent also has the advantage (possessed by diglyme) of forming an azeotropic mixture with water thus facilitating removal of the water formed during the condensation reaction and driving the reaction to higher yields.

The invention also extends to lithium salts of diaminoanthracene whether substituted or not.

In addition to the utility of these materials in the present reaction systems they may have utility as an intermediate or a starting material in other reaction systems.

The present invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples, which show a variety of polycondensation methods, and to the accompanying drawings in which:

Figure 1 is a reaction scheme for Example 11,
Figure 2 is an IR spectra for the product of Example 4B,
Figure 3 is an IR spectra for the product of example 4A,

Figure 4A is a mass spectra for the product of Example 4A taking the base peak as 77,

Figure 4B is the mass spectra for the product of Example 4A with an expanded intensity scale and taking the base peak as 77,

5 Figure 5 is a mass spectra for the product of example 4B1 taking the base peak as 79,

Figure 6A is a mass spectra for the product of Example 11A1 taking the base peak as 160,

10 Figure 6B is the mass spectra for the product of Example 11A1 with an expanded intensity scale and rebased taking the base peak as 249,

Figure 7A is a mass spectra for the product of Example 11A2 taking the base peak as 55,

Figure 7B is the mass spectra for the product of Example 11A2 rebased with the base peak taken as 249,

15 Figure 8A is a mass spectra for the product of Example 11B1 taking the base peak as 160,

Figure 8B is the mass spectra for the product of Example 11B1 rebased taking the base peak as 50, and

20 Figure 9 is a mass spectra for the product of Example 12 taking the base peak as 265.

The conductivity of the polymeric products was measured by the four-probe method on a standard disc of the sample co-polymer. This method is as follows. The powdered polymeric product is compressed into a thin pellet of uniform thickness. A
25 linear spring loaded four probe conductivity cell was used to determine the conductivity. The outer two electrodes are used to measure the current (I), the voltage (V) being measured across the inner two. The volume conductivity is then calculated according to the following equation:

30 resistivity = $\frac{1}{\text{conductivity}}$ = $4.532 \frac{V}{I}$ x thickness of pellet

The four probe method is appropriate for measuring conductivities of the order of $10^{-6} \text{ S cm}^{-1}$ or higher i.e. $10^{-5} \text{ S cm}^{-1}$ and above but requires excessive voltages to be used for measuring lower conductivities in order to produce current values which can be accurately measured.

- 5 For such lower conductivities we use the standard two probe method. Here a cylindrical disc of the sample to be tested is made by compression of a powder of the material. The disc is located between two brass cylinder electrodes with their contact faces provided with platinum foil contact surfaces. The brass cylinders are of the same diameter as the sample disc. The disc and cylinders are enclosed in a
- 10 screw threaded container which enables them to be urged into tight contact. A known current is passed through the array from face to face of the sample disc and the voltage drop is measured. The conductivity (σ) (sigma) can then be calculated from the equations:

15
$$R = V/I; \quad R = \rho \times \frac{\text{length of disc}}{\text{cross section area of disc}}$$

$$\sigma = \frac{1}{\rho} \text{ S cm}^{-1}$$

- 20 The two probe method involves higher contact resistance than the four probe method and accordingly the four probe method is preferable.

All mass spectra results given herein were carried out using the fast atomic bombardment method.

- 25 The mass spectra measurements were carried out by the fast atomic bombardment method (FAB) using a VG ZAB 2SE machine running FAB with a Xenon saddle field fast atom gun. The matrix was MNOBA.

- 30 The m/e values given below in the examples relate to the fragments which can be produced by break up of the polymer molecules including single, double, triple and longer repeat units. Each of the mass spectra given indicate that polymeric species were present.

- Some of the mass spectra have the scale of the intensity expanded so as to reveal the more rare fragments. Others of the mass spectra have been rebased i.e in some cases the most frequently occurring fragment is taken as having 100% intensity ie as the base peak; in other cases a less frequently occurring fragment e.g.
- 5 a smaller one may be taken to have 100% intensity and the other peaks are recalculated on the new base peak.

Example 1

Preparation of Diaminoanthracene

- 10 This can be prepared by the procedure of Schiedt (J. fur Praktische Chemie N.F. Band 157, 1941, p. 203-224 at 218) as follows:
- 20g of anthraquinone was heated at boiling point with 200ml formamide for 4 hours. The supernatant anthraquinone slowly disappeared while yellow crystals deposited. The solution was cooled, suction filtered and washed thoroughly with
- 15 alcohol. The resultant 9,10-diformylaminoanthracene was recrystallized from formamide giving long yellow crystals mpt 439°C. Chemical analysis for $C_{16}H_{12}O_2N_2$ was calculated N 10.60%, found N10.88%. 40g of KOH was dissolved in 100ml of methanol and 10g of the 9,10 diformylaminoanthracene prepared above was added and formed a deep red brown solution. This was heated at boiling point
- 20 for one hour, when red glistening crystals separated.
- The solution was cooled, suction filtered with the exclusion of air and the crystals washed with methanol. The crystal mass was dissolved in acetone, filtered as necessary and the filtrate carefully mixed with petroleum ether to deposit 9,10 diaminoanthracene as glistening flakes. Recrystallization from acetone gave deep
- 25 red crystals. Chemical analysis for $C_{14}H_{12}N_2$ was calculated C 80.75%, H 5.81%, N 13.44% found C 81.06%, H 5.18%, N 12.47%.

Example 2

Polymerisation of anthraquinone with 9,10-diaminoanthracene using titanium tetrachloride ($TiCl_4$)

- 30 9,10-diaminoanthracene (1.0g; 4.8 mmol) and Dabco (3.23g; 28.8 mmol) were dissolved in 20 ml of orthodichorobenzene (o-DCB) while heating at 90°C. Then

titanium tetrachloride (7.2 mmol) in 10ml of orthodichlorobenzene was added dropwise and then an additional 10ml of the solvent was added into the system. Then anthraquinone (0.99g; 4.8 mmol) was added to the mixture and an extra 20ml of the solvent was added. The reaction mixture was refluxed for 24 hours and then the precipitate was filtered off.

The precipitate was then washed thoroughly with hot orthodichlorobenzene to dissolve the soluble polymer and transfer it into the filtrate. Orthodichlorobenzene was removed from the filtrate under vacuum and the remaining product was purified by dissolving in chloroform and then precipitating it with hexane. This precipitate was treated with methanol and the soluble fraction filtered off to leave a dark green/black precipitate.

The yield of the green/black precipitate was 58%.

Its conductivity was of the order of $10^{-5} \text{ S cm}^{-1}$ measured by the four probe method.

Example 3

Polymerisation by polycondensation of anthraquinone with 9,10-diaminoanthracene using glacial acetic acid.

9,10-diaminoanthracene (prepared as in Example 1) (5g; 24 mmol) was dissolved in 100ml of glacial acetic acid and anthraquinone (5g; 24mmol) was added. The mixture was refluxed for three hours at 116°C . The resultant dark green precipitate was filtered off. This precipitate was washed with distilled water and dried in a vacuum oven. The yield was 74%. The electrical conductivity of this product was 10^{-6} to $10^{-5} \text{ S cm}^{-1}$ as measured by the standard four probe method described above.

Mass spectra analysis by fast atomic bombardment of this product gave the following values (m/e), 209(100), 354(25), 764(2), 1143(2), 1350(1), 1541(0.4), 1790(0.3), 1980(0.4), 2231(0.2), 2525(0.2). This indicates a molecular weight of the order of 2525 representing 12 repeating units.

Mass spectra analysis by fast atomic bombardment is a standard procedure. The sample to be tested is dissolved in a solvent and injected into a tube. This dispersed sample is bombarded with ionised xenon producing fragments of the molecules present in the dispersed sample which fragments are ionized, a spectrum of ions of different mass thus being produced. The number outside the brackets, e.g. 209 in 209 (100) above, is the mass of the fragment. The numbers of each fragment of the same mass is summed and the total of the figure inside the brackets i.e. 100 in 209 (100) is called the intensity. An intensity of (100) is the frequency of occurrence of the most stable ionized fragment which may be the monomeric species, the so called "base peak".

The mass of DAA is 208, so that in this case the "base peak" is close to the monomeric species. The low intensity values e.g. (0.2), indicate the largest species detected and since masses greater than about 2000-2500 are not readily detected by this form of mass spectral analysis, these low intensity values indicate that even larger species can be expected to exist.

Example 4A

Polycondensation of 2- tert-butylantraquinone with 9,10 diaminoanthracene using orthodichlorobenzene

2-Tert-butylantraquinone (1 g; 3.78 mmol) in 4ml of orthodichlorobenzene was added to a solution of 9,10 diaminoanthracene (1 g; 4.8 mmol) in 25ml of orthodichlorobenzene. The mixture was refluxed for 17 hours resulting in a liquid and a black precipitate. The black precipitate was filtered off, thoroughly washed with acetone and dried. The yield was 47%. The electrical conductivity of this product was less than 10^{-10} S cm⁻¹ as measured by the two probe method. IR spectra measured on a KBr disc showed an imine peak at 1610 cm⁻¹ and no carbonyl peak. Figure 3 is an IR spectra for this product.

Chemical analysis for C₃₂ H₂₄ N₂ was calculated C 88.07%, H 5.50%, N 6.42%, found C 76.04%, H 3.97%, N 7.25%, O 1.02%.

Mass spectral analysis of this product gave the following values (m/e) 77(100), 439(2.3), 632(0.7), 1073(0.1), 2115(0.15)

Figures 4A and 4B are mass spectra for this product.

5 Example 4B1

Example 4A was repeated using chlorobenzene instead of dichlorobenzene as the solvent and refluxing the mixture for 4 hours instead of 17 hours. The yield was 5%.

Chemical analysis for $C_{32}H_{24}N_2$ was calculated C 88.07%, H 5.50%,
10 N 6.42%, found C 85.05%, H 4.18%, N 8.12%, O 1.26%.

Mass spectral analysis by fast atomic bombardment of this produce gave the following values (m/e) 79 (100), 439 (4.1), 872(6), 1316 (0.3), 1747 (0.3), 2235 (0.2), 2463 (0.2).

Figure 5 is a mass spectra for the product of this example.

15

Example 4B2

The liquid fraction of the reaction mixture is thought to contain the soluble polymeric species from the reaction. The liquid fraction can be separated into the individual polymer and oligomer species or clusters of species of similar molecular
20 weight by column chromatography using silica gel as the column adsorbent media and diethylether as the eluant solvent. This has been done and unreacted anthraquinone and unreacted DAA have been detected and two bands of polymeric species having different molecular weights as indicated by differing elution times. Each band is thought to be a mixture of different polymeric species. The lower
25 molecular weight band (probably oligomeric) consisted of about 1 gram; the higher molecular weight band (with the longer elution time (hold up time)) consisted of about 0.5 gram of solids.

The higher molecular weight fraction (band) exhibited a conductivity of $1 \times 10^{-5} \text{ S cm}^{-1}$ measured by the four probe method.

The higher molecular weight bands are separable into their individual components by fractionation with eluant solvents of increasing polarity. A series of eluants of increasing polarity which may be used is hexane (low polarity), toluene, diethylether, chloroform and methanol (high polarity).

5

Example 5

Polymerisation of 2-ethylanthraquinone and 9,10 diaminoanthracene using titanium tetrachloride.

Example 2 is repeated using 2-ethyl anthraquinone instead of anthraquinone.

10

Example 6

Polymerisation of 2-methylanthraquinone and 9,10 diaminoanthracene
Example 2 is repeated using 2-methylanthraquinone instead of anthraquinone

15 Example 7

Polymerisation of 2,3-dimethylanthraquinone and 9, 10-diaminoanthracene
Example 2 is repeated using 2,3-dimethylanthraquinone instead of anthraquinone.

Examples 8-10

20 Polycondensation of anthraquinones and 9,10 diaminoanthracene

Example 2 is repeated using sodium anthraquinone (Ex 8), 2, 6-dioctyloxyanthraquinone (Ex 9) and 2,6-dihydroxyanthraquinone (Ex 10) instead of anthraquinone.

25 Example 11A1

Synthesis of poly(anthraquinoneimine) using butyllithium as an initiator.

A dry 100 ml round bottom flask containing a dry magnetic bar was connected to an inert gas system (nitrogen). 9,10 diaminoanthracene (1 g; 4.8 mmol) was dissolved in 25 ml of anhydrous tetrahydrofuran in the flask. The solution was cooled to about
30 -100°C in an acetone – liquid nitrogen bath. Once the system had been cooled down n-butyllithium solution (6.4 ml of a 1.5M n-Bu Li solution in hexane; 9.6 mmol) was

added slowly via a syringe while the solution was stirred under a positive pressure of nitrogen.

Once the whole amount of *n*-BuLi had been added the solution was allowed to warm up to 0°C over about 20 minutes and then this reaction mixture was added to a solution of 2-*tert*-butylanthraquinone dissolved in 10 ml of tetrahydrofuran (1 g; 3.8 mmol).

The whole system was then allowed to warm up to room temperature while stirring over about 15 minutes and kept at room temperature for 1 hour.

The precipitate which was formed was filtered off and washed with a small amount of methanol to remove the *n*-butyl-lithium salt. The yield was 41%.

IR spectra showed an imine peak at 1575 cm⁻¹ (The imine peak can occur in the range 1620 to 1575 and is the C=N stretching frequency, the value varying depending on the environment of the bond.). The IR spectra also showed a carbonyl peak at 1670 cm⁻¹, thought to be due to the presence of unreacted 2-*tert*-butyl anthraquinone.

The product was light green in colour.

Its conductivity was 2.0×10^{-5} S cm⁻¹ as measured by the four probe method.

Mass spectra analysis of this product gave the following values (*m/e*) 160 (100) 425(6), 439(3.4), 1000(1.2), 1184(1), 1567(0.4), 1905(0.3), 1980(0.2).

Figures 6A and 6B are mass spectra for this product.

Example 11A2

The liquid fraction was evaporated to dryness and chemical analysis carried out for C₃₂ H₂₄ N₂ calculated C 88.07%, H 5.50%, N 6.42% found C 75.55%, H 5.60%, N 5.38%.

Mass spectra analysis by fast atomic bombardment of the product gave the following values (*m/e*) 55 (100), 431 (1.0), 1034 (2.5), 1235 (1.5), 2650 (0.1).

Figures 7A and 7B are mass spectra for this product.

Example 11B1

Example 11A1 was repeated except that the final reaction step was refluxing for 5 hours instead of holding at room temperature for 1 hour. The precipitate was produced in 50% yield. Mass spectra analysis by fast atomic bombardment gave the following values (m/e) 160 (100), 313 (33), 424 (2.0), 1548 (2.0), 1820 (1.0), 2041 (0.5). Figure 8A and 8B are mass spectra for this product.

The mass of 1548 represents 7 repeat units; that of 1820, 8 repeat units; and that of 2041, 9 repeat units. The calculated molecular weight of a single repeat unit is 438, thus 424 may represent a single repeat-unit with one methyl group removed from the tert-butyl group. However the fragment represented by the mass 313 has not been identified.

Example 11B2

The liquid fraction contained the remaining 50% of the reaction species and the soluble polymer species.

Example 11C

In a modified version of the procedure of example 11A or 11B the cooling is done with a solid carbon dioxide/acetone mixture to achieve a temperature of -70°C to -80°C.

Attached as Figure 1 is a reaction scheme which is believed to set out what occurs in the procedure of Example 11. Figure 1 is a theoretical explanation of what is believed to be occurring but the invention is not dependent on the accuracy or otherwise of the reaction scheme shown in Figure 1.

In Figure 1 compound I.I is 9,10 diaminoanthracene which on reaction with n-BuLi produces a diaminoanthracene dilithium salt compound I.II. This reacts with AQ (compound I.III) to form a transient intermediate compound (I.IV) which in the presence of the protons released during the reaction between I.II and I.III relinquishes the Lithium atoms to form compound (I.V). This on refluxing loses water to produce the poly(anthraquinonimine) compound (I.VI).

Example 12

Example 11 is repeated but replacing the tetrahydrofuran as the reaction medium by diglyme (2-methoxy ethyl ether) by adding diglyme to the reaction mixture at the stage of formation of compound I.II and I.III and distilling off the tetrahydrofuran. Compound I.V was refluxed in the presence of benzene so as to remove the water produced as the benzene/water azeotropic mixture, so as to produce compound I.VI.

IR spectra showed peaks at 1665cm^{-1} and 1580cm^{-1} , the former value is characteristic of C=C aromatic bonds and the latter value is the imine peak.

The conductivity of the product was of the order of 10^{-5} S cm^{-1} as measured by the four probe method. Mass spectral analysis of the product gave the following values (m/e) 265(100), 424(8), 535(13), 696(2.0), 941(1.0) 1337(0.3), 1842(0.1), 1960(0.1) 2214(0.1). Figure 9 is the mass spectra for this product.

Example 13

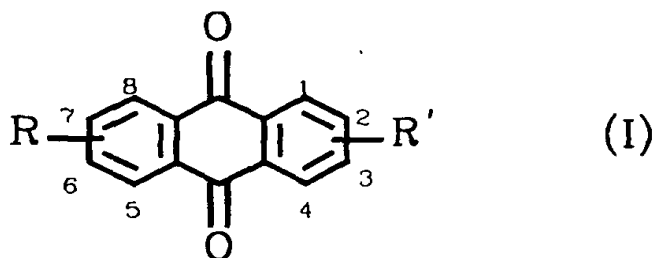
Reduction with NaBH_4

The polymeric products of Examples 2 to 12 are reduced with sodium borohydride in methanol (reflux 18 hours) to give the partially reduced polymer.

CLAIMS

1. The polymeric or oligomeric product obtainable from the reaction of an
 5 anthraquinone with an aromatic diamine, characterised in that the
 anthraquinone is substituted or is not substituted and in that the diamine is a
 diamino anthracene which is substituted or is not substituted.
2. A product as claimed in claim 1 characterised in that the substitution is such
 10 that the product is a homopolymer or homo-oligomer.
3. A product as claimed in claim 1 characterised in that the substitution is such
 that the product is a co-polymer or a co-oligomer.
- 15 4. A product as claimed in claim 1, 2 or 3 characterised in that the
 diaminoanthracene is a 9,10-diaminoanthracene.
5. A product as claimed in claim 1, 3 or 4 characterised in that the anthraquinone
 is of the general formula (I):

20

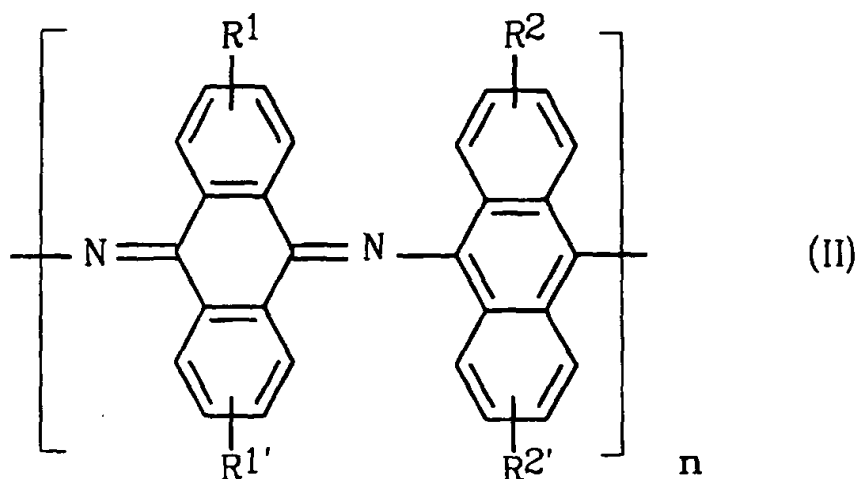


where, R may be the same as or different to R', and may be a hydrogen atom
 (when R = R' = H, the compound is anthraquinone), or CH₃, CH₃CH₂-,
 25 -OCH₃,

-OCH₂CH₃, -CH₂OCH₃, -CH₂OCH₂CH₂OCH₃, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, Br, CN or NO₂, -CH₂COOR or -CH₂NHCOR'' (where R'' is C₁ - C₆ alkyl or a phenyl or biphenyl group).

- 5 6. A product as claimed in any one of claims 1 to 5 characterised in that the ratio of anthraquinone to aromatic diamine is in the range 5:1 to 1:5.
7. A product as claimed in any preceding claim, characterised in that the ratio of anthraquinone to aromatic diamine is in the range 3:1 to 1:3.
- 10 8. A product as claimed in any preceding claim, characterised in that the ratio of anthraquinone to aromatic diamine is in the range 2:1 to 1:2.
- 15 9. A product as claimed in any one of claims 1 to 8 characterised in that the anthraquinone is a C₁ - C₆ alkyl anthraquinone or a C₁ - C₁₀ alkoxy anthraquinone or a hydroxyanthraquinone.
- 20 10. A product as claimed in claim 9 characterised in that the anthraquinone is 2-ethyl anthraquinone or 2-methyl anthraquinone, or 2,3-dimethyl anthraquinone or 2,6-diethyloxy anthraquinone or 2,6-dihydroxyanthraquinone.

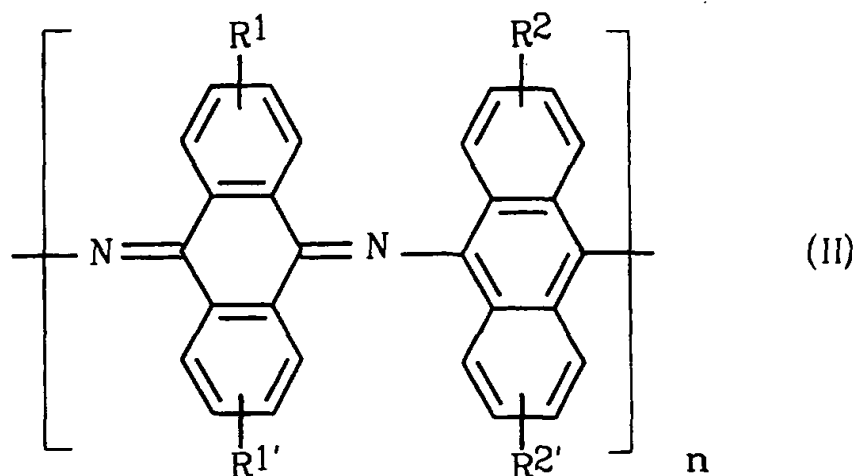
11. A product as claimed in claim 1 having the general formula II



5 where, R^1 may be the same as or different to $R^{1'}$, which may be the same as or different to R^2 , which may be the same as or different to $R^{2'}$ and each of R^1 , $R^{1'}$, R^2 , and $R^{2'}$ is a hydrogen atom or CH_3 , $\text{CH}_3\text{CH}_2\text{-OCH}_3$, $\text{-OCH}_2\text{CH}_3$, $\text{-CH}_2\text{OCH}_3$, $\text{-CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, Br, CN or NO_2 , $\text{-CH}_2\text{COOR}$ or $\text{-CH}_2\text{NHCOR}'''$ (where R''' is C_1 - C_6 alkyl or a phenyl or biphenyl group), or a C_1 - C_3 alkyl

10 group, or an aryl group e.g. a benzyl group, or an $\text{-SO}_3\text{H}$ group or a hydroxyl group or a C_1 - C_3 alkoxy group or an H_2PO_3 group, and R^1 and $R^{1'}$ are different to R^2 and $R^{2'}$ and n is an integer ranging from 2 to 100 preferably 10 to 100.

12. A product as claimed in claim 1 having the general formula II



5 where, R^1 may be the same as or different to $R^{1'}$, and each of R^1 and $R^{1'}$ is a hydrogen atom or CH_3 , CH_3CH_2 , $-OCH_3$, $-OCH_2CH_3$, $-CH_2OCH_3$, $-CH_2OCH_2CH_2OCH_3$, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, Br, CN or NO_2 , $-CH_2COOR$ or $-CH_2NHCOR'''$ (where R''' is $C_1 - C_6$ alkyl or a phenyl or biphenyl group), and R^2 may be the same or different to $R^{2'}$ and each of R^2 and $R^{2'}$ is a hydrogen atom or a $C_1 - C_3$ alkyl group, or an
 10 aryl group e.g. a benzyl group, or an $-SO_3H$ group or a hydroxyl group or a $C_1 - C_3$ alkoxy group or an H_2PO_3 group, and R^1 and $R^{1'}$ are different to R^2 and $R^{2'}$ and n is an integer ranging from 2 to 100 preferably 10 to 100.

15 13. A product as claimed in claim 11 or claim 12 characterised in that R^1 is the same as $R^{1'}$ but is different from R^2 and $R^{2'}$ and in that R^2 and $R^{2'}$ are the same.

14. A product as claimed in claim 11 or claim 12 characterised in that R^1 is the same as $R^{1'}$ and as R^2 and $R^{2'}$ but is not hydrogen.

5 15. A product as claimed in claim 11 or claim 12 characterised in that R^1 is different from $R^{1'}$ and R^2 is different from $R^{2'}$ and R^1 and $R^{1'}$ are both different from R^2 and $R^{2'}$.

10 16. A product as claimed in any one of claims 11 to 14 characterised in that R^1 and R^2 are not hydrogen and in that $R^{1'}$ and $R^{2'}$ are not the same

17. Poly (9-aminoanthracenes) as claimed in claim 1 characterised in that they have an oxidation state between 0.25 to 0.75, and a formula (III) at an oxidation state 0.25, a formula (IV) at an oxidation state 0.5 and a formula (V) at an oxidation state 0.75 as follows

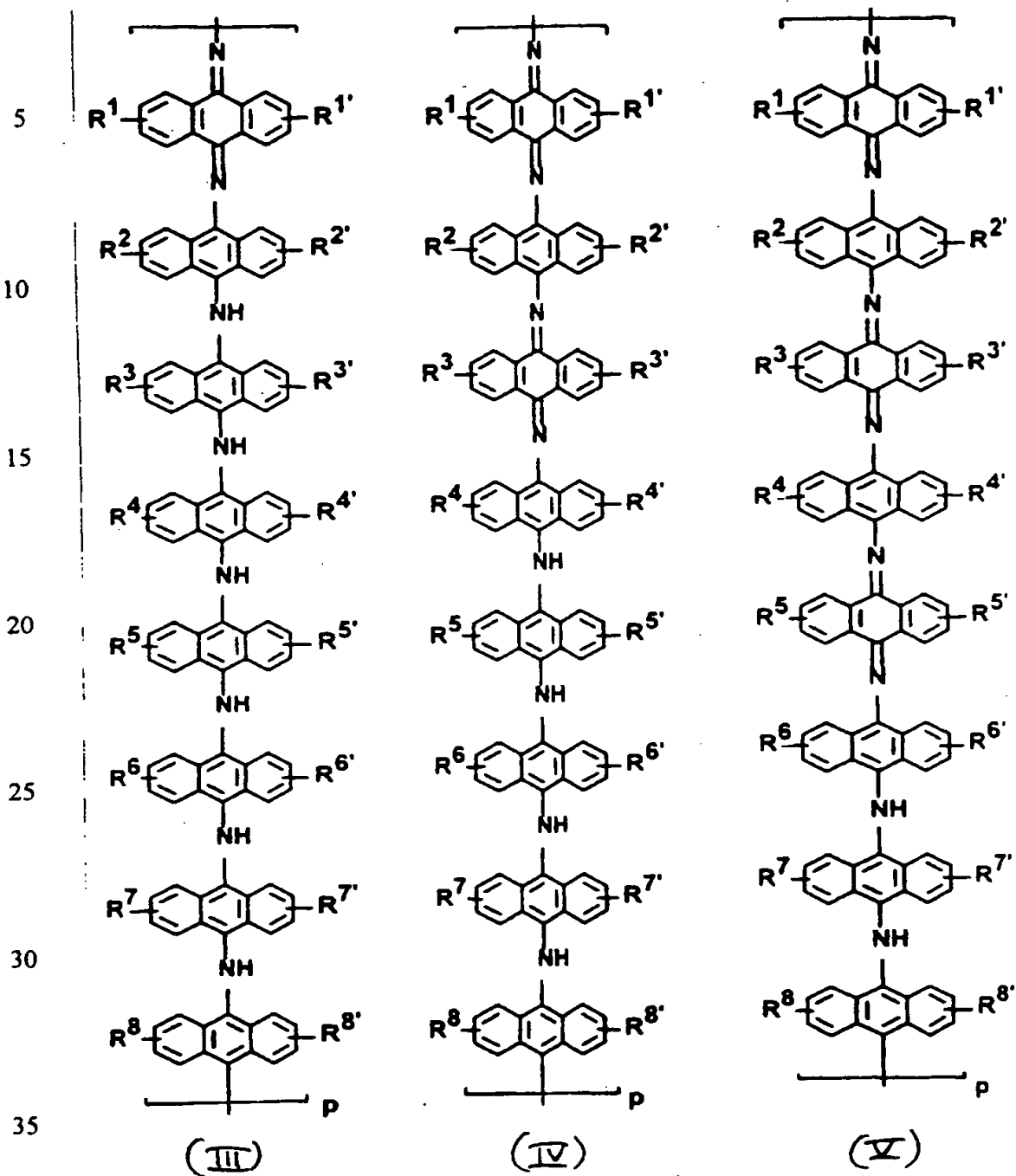
15

20

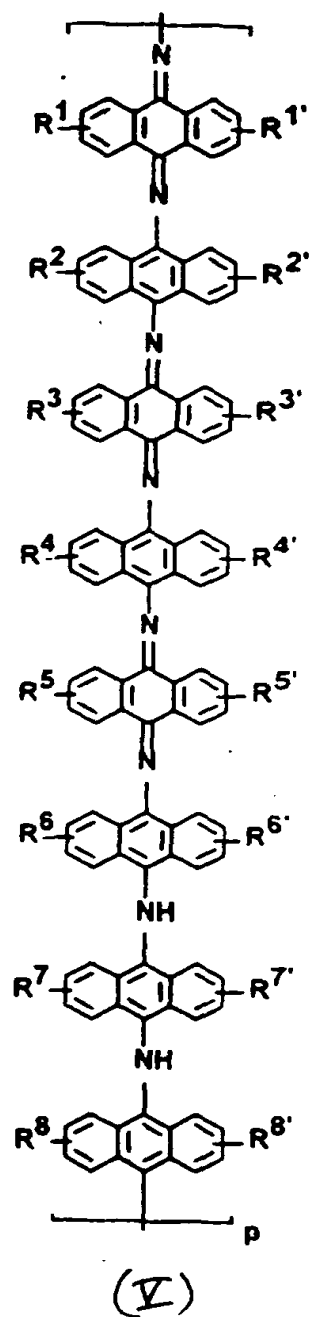
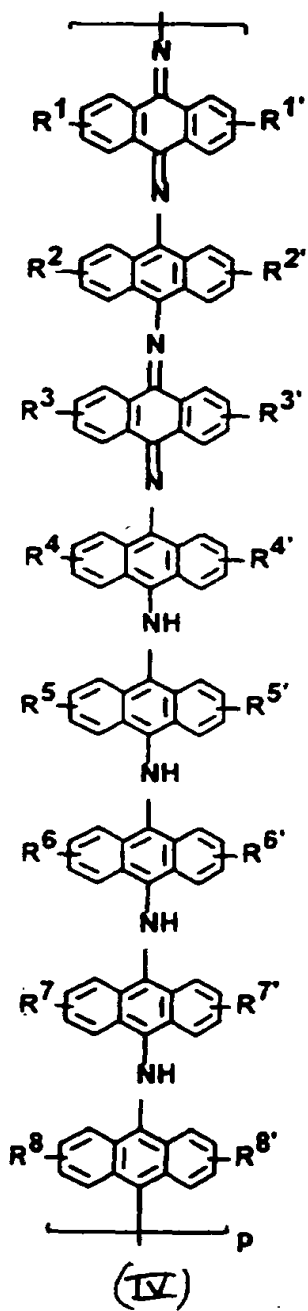
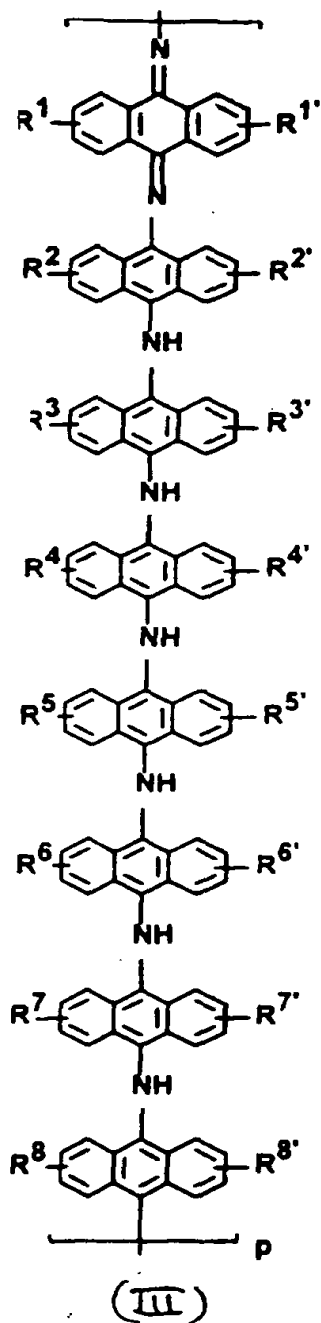
25

30

35



18. Poly (9-aminoanthracenes) as claimed in claim 1 characterised in that they have an oxidation state between 0.25 to 0.75, and a formula (III) at an oxidation state 0.25 , a formula (IV) at an oxidation state 0.5 and a formula (V) at an oxidation state 0.75 as follows



in which the R groups are the same as the R' groups and the R groups are all the same;

or

5 the R groups are the same as the R' groups and the R¹, R³, R⁵ and R⁷ groups are all the same and the R², R⁴, R⁶ and R⁸ groups are all the same but are different to the R¹, R³, R⁵ and R⁷ groups;

or

10 the R groups are different to the R' groups and the R¹, R³, R⁵ and R⁷ groups are all the same and the R², R⁴, R⁶ and R⁸ groups are all the same but are different to the R¹, R³, R⁵ and R⁷ groups.

19. A method of production of a homopolymer or copolymer or homo-oligomer or co-oligomer product characterised in that the product is obtained by
15 condensation of an anthraquinone, substituted or not with a diaminoanthracene, substituted or not.

20. A method as claimed in claim 19 characterised in that the polycondensation uses a titanium compound.

20

21. A method as claimed in claim 20, characterised in that the titanium compound is selected from titanium tetrachloride and titanium alkoxides e.g. titanium tetraisopropoxide or titanium tetra-n-butoxide.

25 22. A method as claimed in any one of claims 19 to 21, characterised in that the diamino anthracene is dissolved in a suitable solvent and is heated with the titanium compound, the anthraquinone compound is added to the mixture and the mixture is stirred and heated e.g. for a period in excess of

12 hours, the mixture is filtered and the residue is washed and the product is purified.

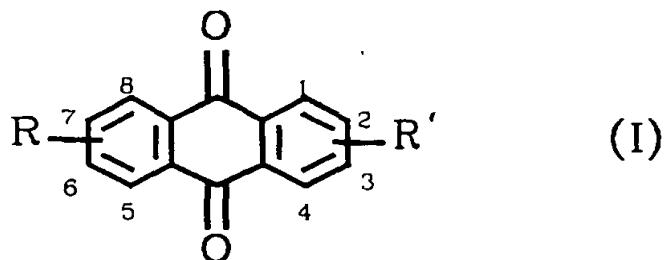
- 5 23. A transparent electroconductive coating comprising a product as claimed in any one of claims 1 to 18.
24. A static shielding material comprising a product as claimed in any one of claims 1 to 18.
- 10 25. A process for making copolymers characterised in that it comprises reacting a lithium salt of diaminoanthracene, substituted or not, with an anthraquinone substituted or not.
- 15 26. A process as claimed in claim 25 characterised in that anthraquinone, substituted or not, is heated with diamino anthracene, substituted or not, in the absence of a catalyst or any other species used to facilitate condensation.
- 20 27. A process as claimed in claim 25 characterised in that diaminoanthracene, substituted or not, is reacted in a solvent under inert gas with an organolithium compound e.g. n-butyllithium or lithium diisopropyl amide, at low temperature, at which the resulting lithium diaminoanthracene salt is stable, preferably -70°C or lower, but above the freezing point of the
- 25 reaction mixture, to produce diaminoanthracene lithium salt, the temperature of the reaction mixture is then allowed to rise, e.g. to at least -20°C , preferably to room temperature and the reaction mixture is then added to anthraquinone, substituted or not, and the reaction allowed to

Amendments to the claims have been filed as follows

CLAIMS

1. The polymeric or oligomeric product obtainable from the reaction of an
5 anthraquinone with an aromatic diamine, characterised in that the
anthraquinone is substituted or is not substituted and in that the diamine is a
diamino anthracene which is substituted or is not substituted.
2. A product as claimed in claim 1 characterised in that the substitution is such
10 that the product is a homopolymer or homo-oligomer.
3. A product as claimed in claim 1 characterised in that the substitution is such
that the product is a co-polymer or a co-oligomer.
- 15 4. A product as claimed in claim 1, 2 or 3 characterised in that the
diaminoanthracene is a 9,10-diaminoanthracene.
5. A product as claimed in claim 1, 3 or 4 characterised in that the anthraquinone
is of the general formula (I):

20

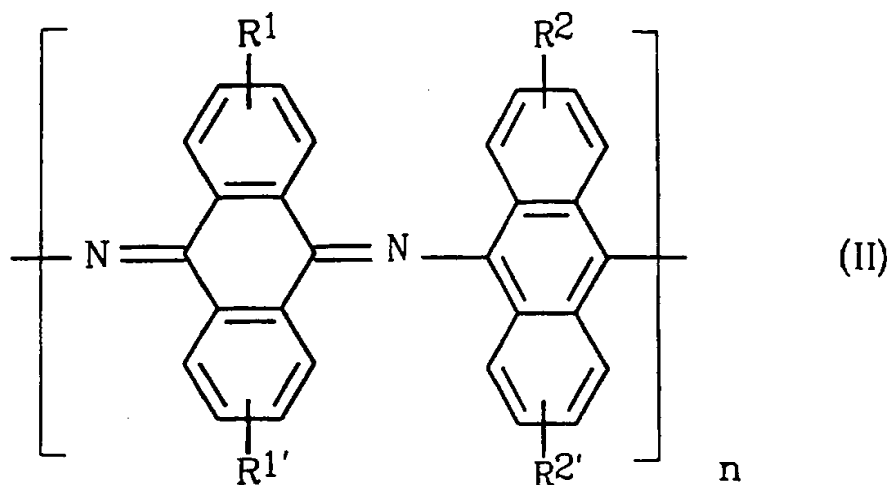


where, R may be the same as or different to R', and may be a hydrogen atom
(when R = R' = H, the compound is anthraquinone), or CH₃, CH₃CH₂-,
25 -OCH₃,

-OCH₂CH₃, -CH₂OCH₃, -CH₂OCH₂CH₂OCH₃, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, Br, CN or NO₂, -CH₂COOR or -CH₂NHCOR" (where R" is C₁ - C₆ alkyl or a phenyl or biphenyl group).

- 5 6. A product as claimed in any one of claims 1 to 5 characterised in that the ratio of anthraquinone to aromatic diamine is in the range 5:1 to 1:5.
7. A product as claimed in any preceding claim, characterised in that the ratio of anthraquinone to aromatic diamine is in the range 3:1 to 1:3.
- 10 8. A product as claimed in any preceding claim, characterised in that the ratio of anthraquinone to aromatic diamine is in the range 2:1 to 1:2.
- 15 9. A product as claimed in any one of claims 1 to 8 characterised in that the anthraquinone is a C₁ - C₆ alkyl anthraquinone or a C₁ - C₁₀ alkoxy anthraquinone or a hydroxyanthraquinone.
- 20 10. A product as claimed in claim 9 characterised in that the anthraquinone is 2-ethyl anthraquinone or 2-methyl anthraquinone, or 2,3-dimethyl anthraquinone or 2,6-diethyloxy anthraquinone or 2,6-dihydroxyanthraquinone.

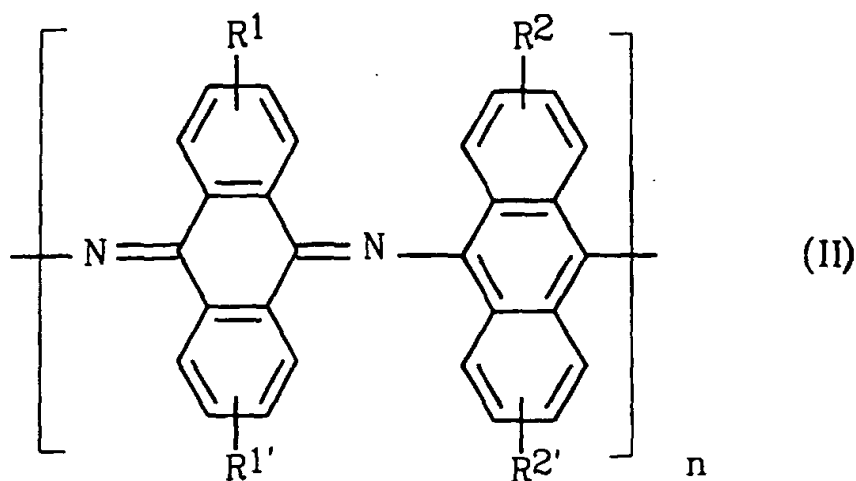
11. A product as claimed in claim 1 having the general formula II



5 where, R^1 may be the same as or different to $R^{1'}$, which may be the same as or different to R^2 , which may be the same as or different to $R^{2'}$ and each of R^1 , $R^{1'}$, R^2 , and $R^{2'}$ is a hydrogen atom or CH_3 , CH_3CH_2 , $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, Br, CN or NO_2 , $-\text{CH}_2\text{COOR}$ or $-\text{CH}_2\text{NHCOR}'''$ (where R''' is $\text{C}_1 - \text{C}_6$ alkyl or a phenyl or biphenyl group), or a $\text{C}_1 - \text{C}_5$ alkyl

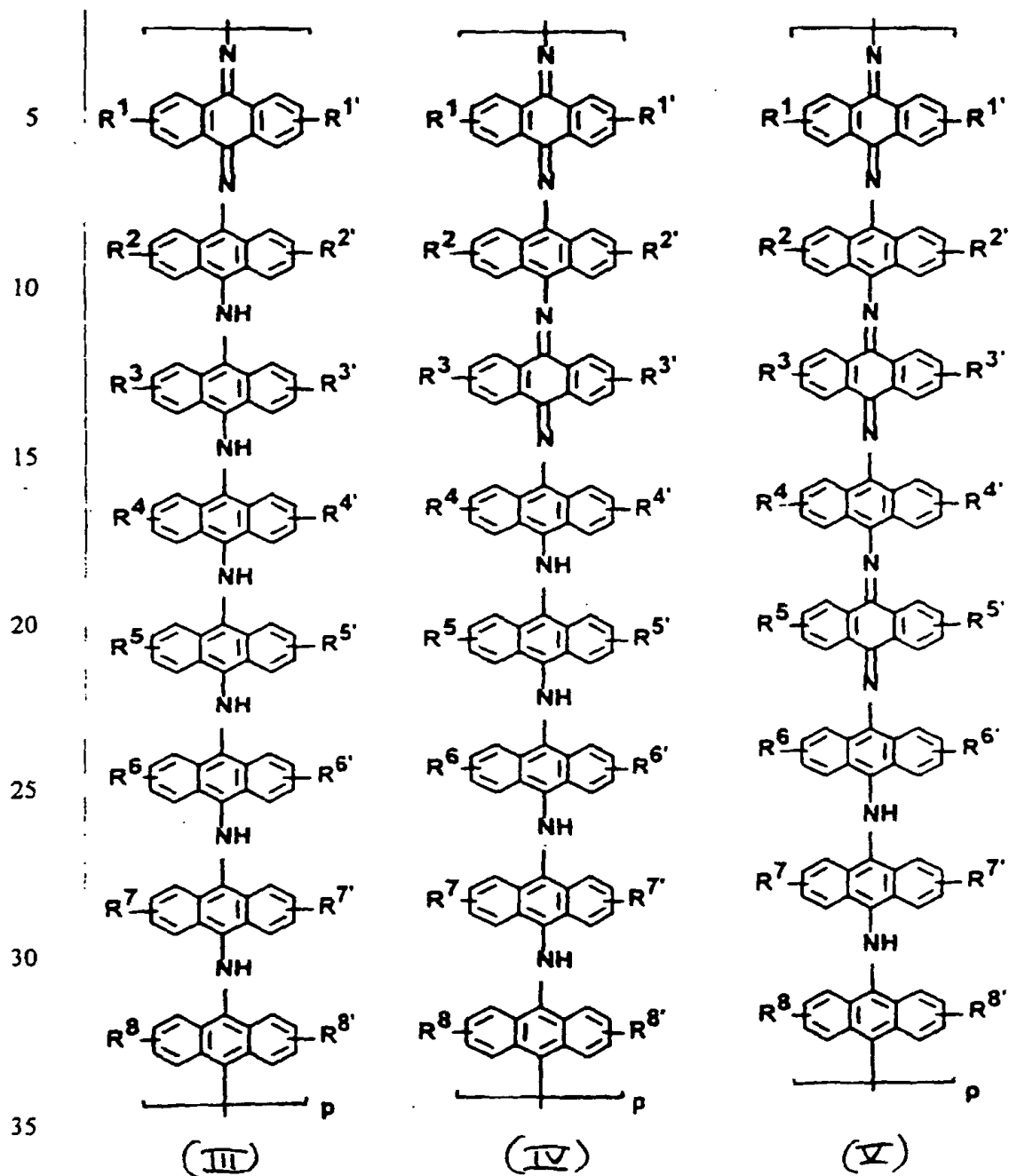
10 group, or an aryl group e.g. a benzyl group, or an $-\text{SO}_3\text{H}$ group or a hydroxyl group or a $\text{C}_1 - \text{C}_5$ alkoxy group or an H_2PO_3 group, and R^1 and $R^{1'}$ are different to R^2 and $R^{2'}$ and n is an integer ranging from 2 to 100 preferably 10 to 100.

12. A product as claimed in claim 1 having the general formula II



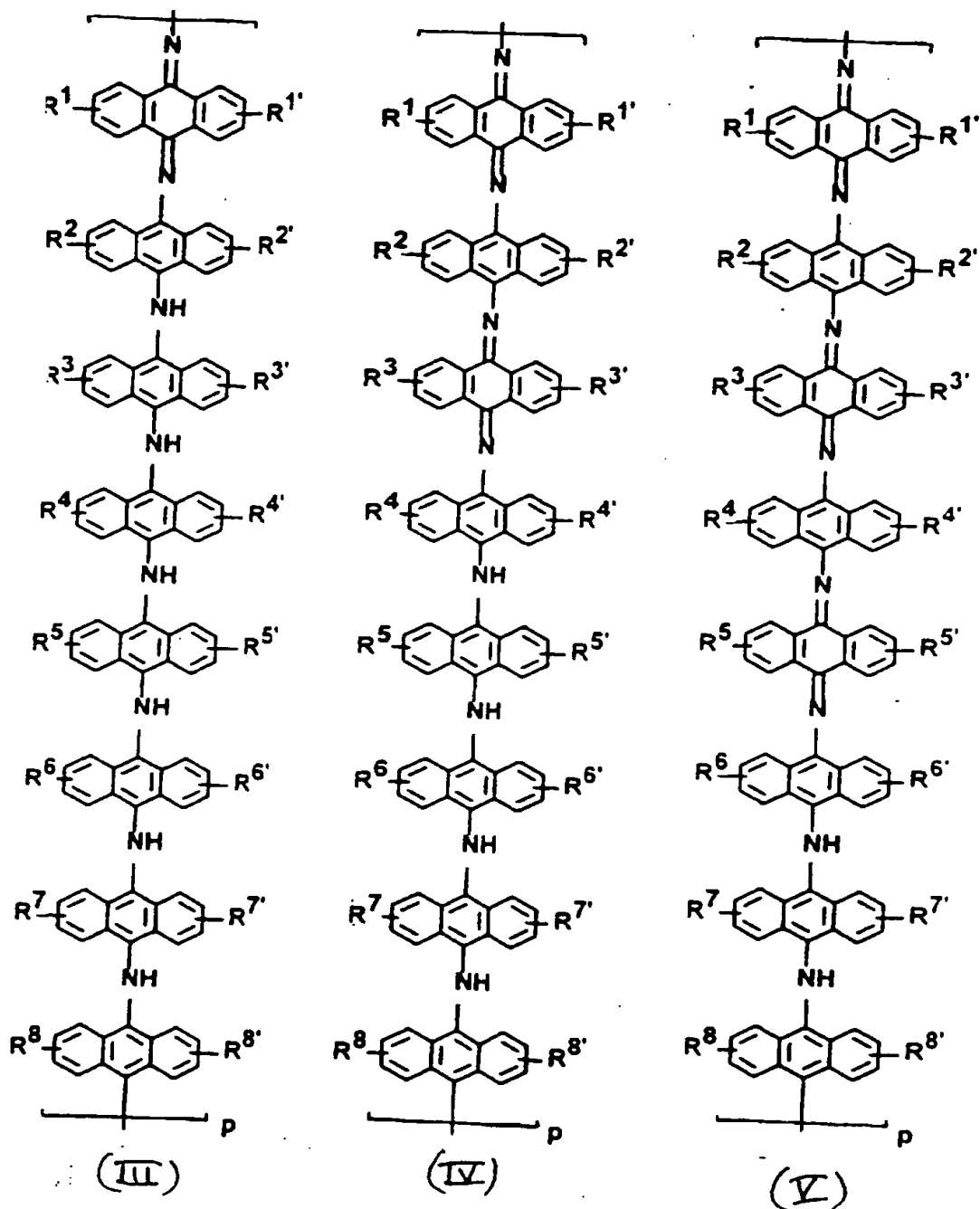
- 5 where, R^1 may be the same as or different to $R^{1'}$, and each of R^1 and $R^{1'}$ is a hydrogen atom or CH_3 , CH_3CH_2 , $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, methoxyethoxyethoxymethyl, aryloxymethyl, phenyl, Cl, Br, CN or NO_2 , $-\text{CH}_2\text{COOR}$ or $-\text{CH}_2\text{NHCOR}'''$ (where R''' is $\text{C}_1 - \text{C}_6$ alkyl or a phenyl or biphenyl group), and R^2 may be the same or different to $R^{2'}$ and each of R^2 and $R^{2'}$ is a hydrogen atom or a $\text{C}_1 - \text{C}_3$ alkyl group, or an
- 10 aryl group e.g. a benzyl group, or an $-\text{SO}_3\text{H}$ group or a hydroxyl group or a $\text{C}_1 - \text{C}_3$ alkoxy group or an H_2PO_3 group, and R^1 and $R^{1'}$ are different to R^2 and $R^{2'}$ and n is an integer ranging from 2 to 100 preferably 10 to 100.
- 15 13. A product as claimed in claim 11 or claim 12 characterised in that R^1 is the same as $R^{1'}$ but is different from R^2 and $R^{2'}$ and in that R^2 and $R^{2'}$ are the same.

14. A product as claimed in claim 11 or claim 12 characterised in that R^1 is the same as $R^{1'}$ and as R^2 and $R^{2'}$ but is not hydrogen.
- 5 15. A product as claimed in claim 11 or claim 12 characterised in that R^1 is different from $R^{1'}$ and R^2 is different from $R^{2'}$ and R^1 and $R^{1'}$ are both different from R^2 and $R^{2'}$.
- 10 16. A product as claimed in any one of claims 11 to 14 characterised in that R^1 and R^2 are not hydrogen and in that $R^{1'}$ and $R^{2'}$ are not the same
- 15 17. Poly (9-aminoanthracenes) as claimed in claim 1 characterised in that they have an oxidation state between 0.25 to 0.75, and a formula (III) at an oxidation state 0.25, a formula (IV) at an oxidation state 0.5 and a formula (V) at an oxidation state 0.75 as follows
- 20
- 25
- 30
- 35



in which R¹ to R⁸ are not all hydrogen.

18. Poly (9-aminoanthracenes) as claimed in claim 1 characterised in that they have an oxidation state between 0.25 to 0.75, and a formula (III) at an oxidation state 0.25, a formula (IV) at an oxidation state 0.5 and a formula (V) at an oxidation state 0.75 as follows



in which the R groups are the same as the R' groups and the R groups are all the same;

or

- 5 the R groups are the same as the R' groups and the R¹, R³, R⁵ and R⁷ groups are all the same and the R², R⁴, R⁶ and R⁸ groups are all the same but are different to the R¹, R³, R⁵ and R⁷ groups;

or

- 10 the R groups are different to the R' groups and the R¹, R³, R⁵ and R⁷ groups are all the same and the R², R⁴, R⁶ and R⁸ groups are all the same but are different to the R¹, R³, R⁵ and R⁷ groups.

19. A method of production of a homopolymer or copolymer or homo-oligomer or co-oligomer product characterised in that the product is obtained by
15 condensation of an anthraquinone, substituted or not with a diaminoanthracene, substituted or not.

20. A method as claimed in claim 19 characterised in that the polycondensation
20 uses a titanium compound.

21. A method as claimed in claim 20, characterised in that the titanium
compound is selected from titanium tetrachloride and titanium alkoxides
e.g. titanium tetraisopropoxide or titanium tetra-n-butoxide.

- 25 22. A method as claimed in any one of claims 19 to 21, characterised in that the diamino anthracene is dissolved in a suitable solvent and is heated with the titanium compound, the anthraquinone compound is added to the mixture and the mixture is stirred and heated e.g. for a period in excess of

12 hours, the mixture is filtered and the residue is washed and the product is purified.

23. A transparent electroconductive coating comprising a product as claimed in
5 any one of claims 1 to 18.
24. A static shielding material comprising a product as claimed in any one of
claims 1 to 18.
- 10 25. A process for making copolymers characterised in that it comprises reacting
a lithium salt of diaminoanthracene, substituted or not, with an
anthraquinone substituted or not.
- 15 26. A process as claimed in claim 25 characterised in that anthraquinone,
substituted or not, is heated with diamino anthracene, substituted or not, in
the absence of a catalyst or any other species used to facilitate
condensation.
- 20 27. A process as claimed in claim 25 characterised in that diaminoanthracene,
substituted or not, is reacted in a solvent under inert gas with an
organolithium compound e.g. n-butyllithium or lithium diisopropyl amide,
at low temperature, at which the resulting lithium diaminoanthracene salt is
stable, preferably -70°C or lower, but above the freezing point of the
25 reaction mixture, to produce diaminoanthracene lithium salt, the
temperature of the reaction mixture is then allowed to rise, e.g. to at least -
 20°C , preferably to room temperature and the reaction mixture is then
added to anthraquinone, substituted or not, and the reaction allowed to

occur, preferably at elevated temperature, e.g. by refluxing, to remove the water produced in the condensation reaction from the reaction mixture.

28. Lithium salts of diaminoanthracene, whether substituted or not.



Application No: GB 9912841.5
Claims searched: 1-17

Examiner: Martin Price
Date of search: 24 September 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.Q): C3R - RSM

Int CI (Ed.6): C08G 73/00, 73/02

Other: Online - WPI, EPODOC, PAJ, CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0295676 A2 (BASF)	
A	EP 0053937 A1 (Asahi-Dow)	
A	US 4102873 (US Navy)	
A	WPI Accession number 91-129168[18] & JP 3068623 (Fuji) - see abstract	
A	J. Polym. Sci., Polym. Chem. Ed., 1985, 23(11), 2779-90, Frazer et al: see CAS Accession number 1986:130374	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

